

INTERPRETING  
*organic*  
*spectra*

D. WHITTAKER



## Interpreting Organic Spectra



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## Preface

This book, like many other text-books, has its origins in a course given by the author. The course was for beginners in spectroscopy; it was a conventional series of lectures on techniques, with tutorials spent interpreting spectra. This quickly proved that while lecturing is a good way of teaching spectroscopy, lectures on how to interpret spectra have something in common with lectures on how to ride a bicycle. Since most organic chemists regard spectroscopy as a means of gaining structural information about compounds in which they are interested, the course was modified to become a series of workshops, in which a short lecture on a technique was followed by many examples to interpret, while post-graduate students helped with early difficulties. This resulted in a big improvement in the ability of students to get structural data out of spectra, and made the post-graduates wish that they had learned spectroscopy this way, but the exercises in combining the results of all the techniques were less successful. This book aims to correct this problem and is the course I would choose to teach if sufficient workshops were available. It tries to show that each technique has a particular speciality, and that these need to be combined to identify a structure which is consistent with all the spectra.

In a course like this, the question of how much to write about a technique is debatable. One extreme would be to consider only the spectra, and to ignore how they are produced; the other is to delve too deeply into the theory of the method, and leave the student uncertain what to look for in the actual spectrum. I have aimed to be closer to the first extreme than the second, since some excellent detailed books on spectroscopy are available. The theory parts of this book cover approximately the same ground as the video tapes on IR, MS, UV,  $^{13}\text{C}$  and  $^1\text{H}$  spectra which were made at the University of Liverpool and which are available from the Royal Society of Chemistry.

The spectra should also be useful to teachers who are not trying to teach all the areas of spectroscopy covered here. In many cases, the mass spectrum can be replaced by a molecular formula, though this substantially increases the difficulty of a few problems. Many  $^{13}\text{C}$  problems can be solved without  $^1\text{H}$ , and *vice versa*, though this will make a few problems too difficult for beginners.

Compiling a collection of spectra like this has required a lot of help, and I am particularly grateful for the help of Sandra Hedges, Ann Leyden, Steve Apter and Allan Mills in running most of them. Thanks are also due to Frank Doran, who discovered samples in remote corners of the Chemistry Department, and Dr. J. A. Race of Micromass, who was very helpful with mass spectrometry. Finally, I must thank Frances Poole, for typing the manuscript.

David Whittaker





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## Infrared Spectroscopy

Infrared spectroscopy is the best means of identifying functional groups in a molecule. It involves measuring the absorption by a substance of radiation in the region from  $4000$  to  $600\text{ cm}^{-1}$ . The range covers roughly  $2.5\text{--}16\text{ }\mu\text{m}$  ( $1\text{ }\mu\text{m} = 10^{-4}\text{ cm}$ ), but the frequency scale is now used universally.

Every bond in a molecule vibrates, resulting in a change in its dipole moment. This change in dipole moment provides a mechanism for the absorption of radiation. The energy of the vibration is such that the radiation absorbed is in the infrared region, which is of lower frequency, and hence lower energy, than visible light. Consequently, every bond in a molecule has an absorption peak in the infrared spectrum or the Raman spectrum of the molecule. Every substance therefore has its own unique infrared spectrum, so that we can identify any organic material by comparing its infrared spectrum with that of a known sample. In addition, each different functional group, such as O–H, C–H or C=C, absorbs within a narrow range of frequencies so that we can identify a functional group present in a molecule by the presence of an absorption band in a particular range of the infrared spectrum.

The frequency at which a bond absorbs radiation depends on the masses of the atoms forming the bond. The bonds which absorb radiation at the upper end of the frequency range are those which involve a light atom, hydrogen, with a heavier atom, such as nitrogen, oxygen or carbon. Hydrogen, being light, vibrates strongly and rapidly, so we see a strong, high energy absorption. As we move to lower frequencies, we come to the vibrations of two heavier atoms, such as C–N, C–O and C–C, and finally, at the lowest energies, we find the vibrations of the heavier atoms bonded to very heavy atoms, such as C–Cl, C–Br and C–I. Within this general trend, multiple bonds absorb higher energy radiation than single bonds, so the C $\equiv$ C bond absorbs at higher frequency than the C=C bond.

Before we study an infrared spectrum, we should consider how it is obtained. The sample to be studied is usually examined in one of four ways:

- (1) As a pure liquid.
- (2) As a mull. This method is used for solids. The solid is ground finely using a pestle and mortar, and mixed with a small amount of a liquid hydrocarbon (liquid paraffin) and run as a liquid. This has the disadvantage that the spectrum of the liquid hydrocarbon is superimposed on the spectrum of the sample.
- (3) The compound is finely ground, mixed with KBr, compressed and run as a disc. This avoids adding extra absorption, but is time consuming.
- (4) The compound is dissolved in a suitable solvent, and run as a solution. The spectrum cannot be observed in regions where the solvent absorbs.

Now let us consider an infrared spectrum. The spectrum of phenylamine, PhNH<sub>2</sub> (also known as aniline), is shown in Figure 1.1.

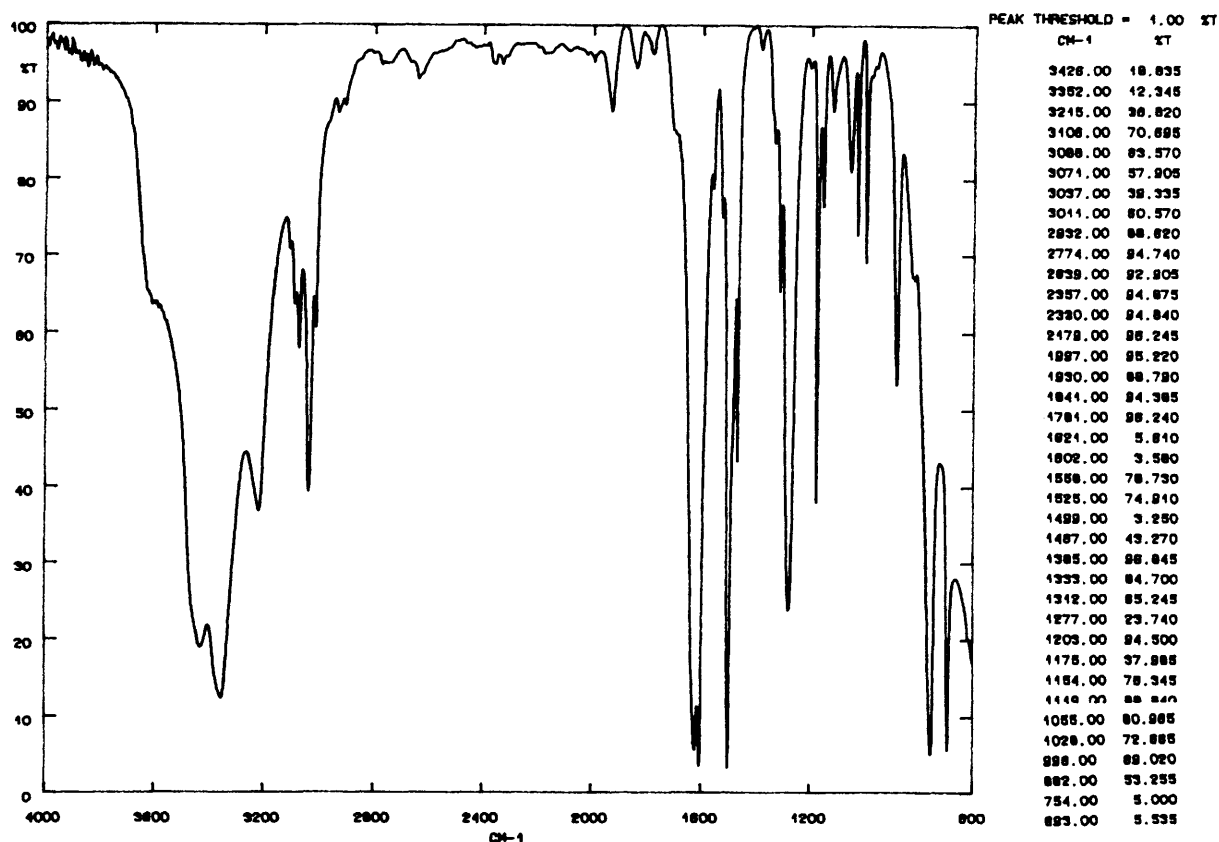
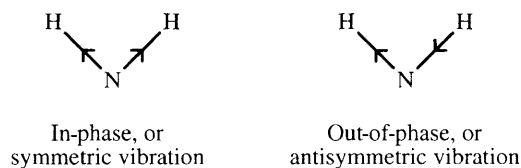


Figure 1.1

The spectrum records the amount of radiation transmitted at each frequency, so the maximum absorption occurs when the least light is transmitted, and the recorder line is closest to the bottom of the spectrum. Positions of maximum absorption are difficult to measure accurately from the spectrum, so most spectrometers record them automatically, and print them alongside the spectrum, giving the % of radiation transmitted (%T) alongside. The machine can be set to record frequencies of all or only the stronger peaks.

Phenylamine has an  $\text{-NH}_2$  group, which characteristically absorbs in the region from  $3500$  to  $3250\text{ cm}^{-1}$ . The spectrum actually has two peaks in this range, at  $3426$  and  $3352\text{ cm}^{-1}$ . These do NOT represent a peak for each N-H bond (the bonds are indistinguishable so must have identical absorption frequencies): they result from the in-phase and out-of-phase vibrations of the N-H bonds:



If the N-H bond is part of an amide, hydrogen bonding moves the absorption to lower frequency. If we have a secondary amine, with only one N-H bond, we obtain a single peak, which can easily be confused with the O-H bond.

A genuine O-H bond is shown in the next spectrum, that of butan-2-ol,  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ . This is shown in Figure 1.2. The O-H bond absorbs

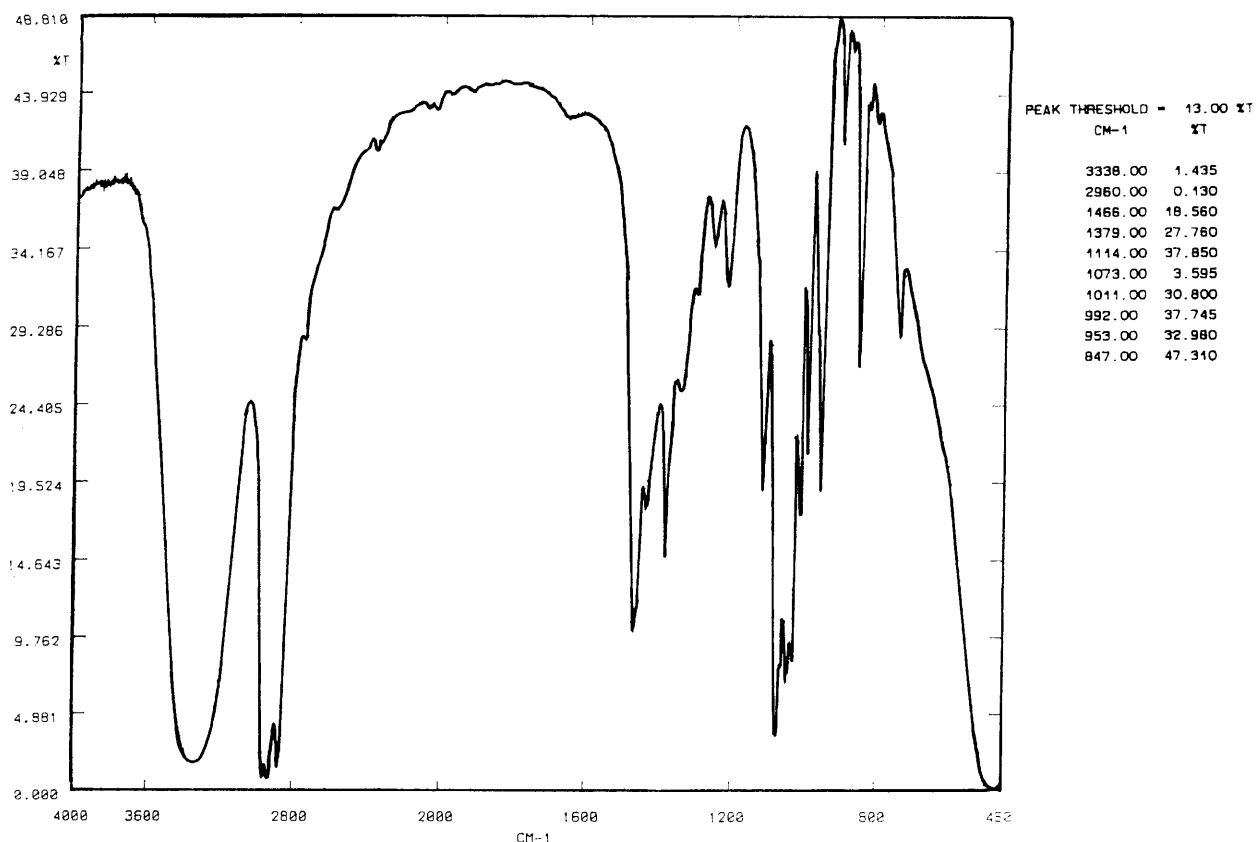
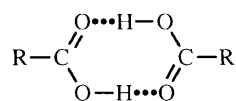


Figure 1.2

radiation in the range  $3700\text{--}3200\text{ cm}^{-1}$ , and we find that butan-2-ol has a peak at  $3338\text{ cm}^{-1}$ . The O–H peak, like the N–H peak but unlike other peaks in the spectrum, is a broad rounded peak rather than the usual sharp spiked peaks. This is a result of intermolecular hydrogen bonding. The hydrogen atom on any particular oxygen atom is probably attached to another oxygen atom by hydrogen bonding, so bond vibrations vary over a frequency range, and the broad peak which we see is an envelope covering many absorptions at slightly different frequencies. If we dilute the sample of butan-2-ol with solvent which cannot form a hydrogen bond, such as dichloromethane, we get the spectrum shown in Figure 1.3, in which the broad O–H bond peak is reduced, and a small sharp absorption peak has appeared at higher frequency, resulting from the non-hydrogen bonded O–H bond. At greater dilution of the alcohol dissolved in dichloromethane, the original O–H peak has almost vanished, and the non-hydrogen bonded peak has further increased in size, as shown in Figure 1.4.

The O–H bond of a carboxylic acid shows even stronger hydrogen bonding than that of an alcohol, since the acid is so strongly hydrogen bonded as to exist in the dimeric form in the pure liquid:



As a result, the carboxylic acid O–H group has an extremely broad absorption peak in the range  $3200\text{--}2200\text{ cm}^{-1}$ . Combined with a carbonyl peak in the range  $1725\text{--}1680\text{ cm}^{-1}$ , this makes identification of a carboxylic acid from its

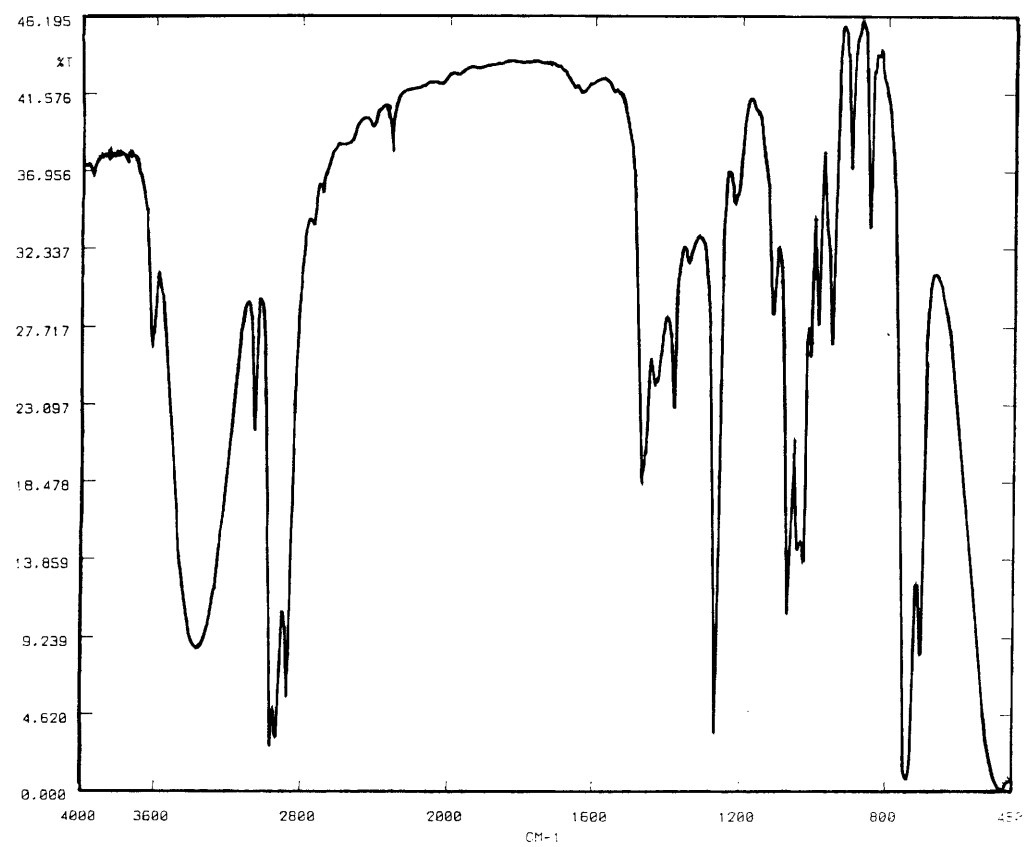


Figure 1.3

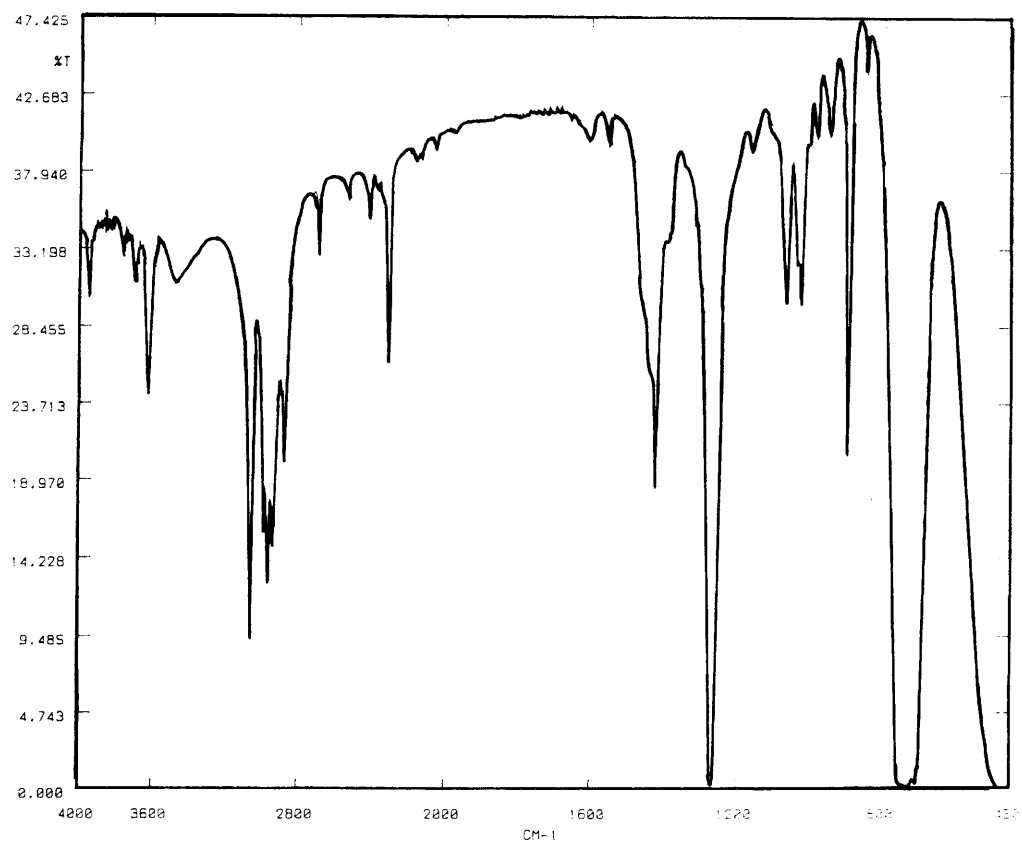


Figure 1.4

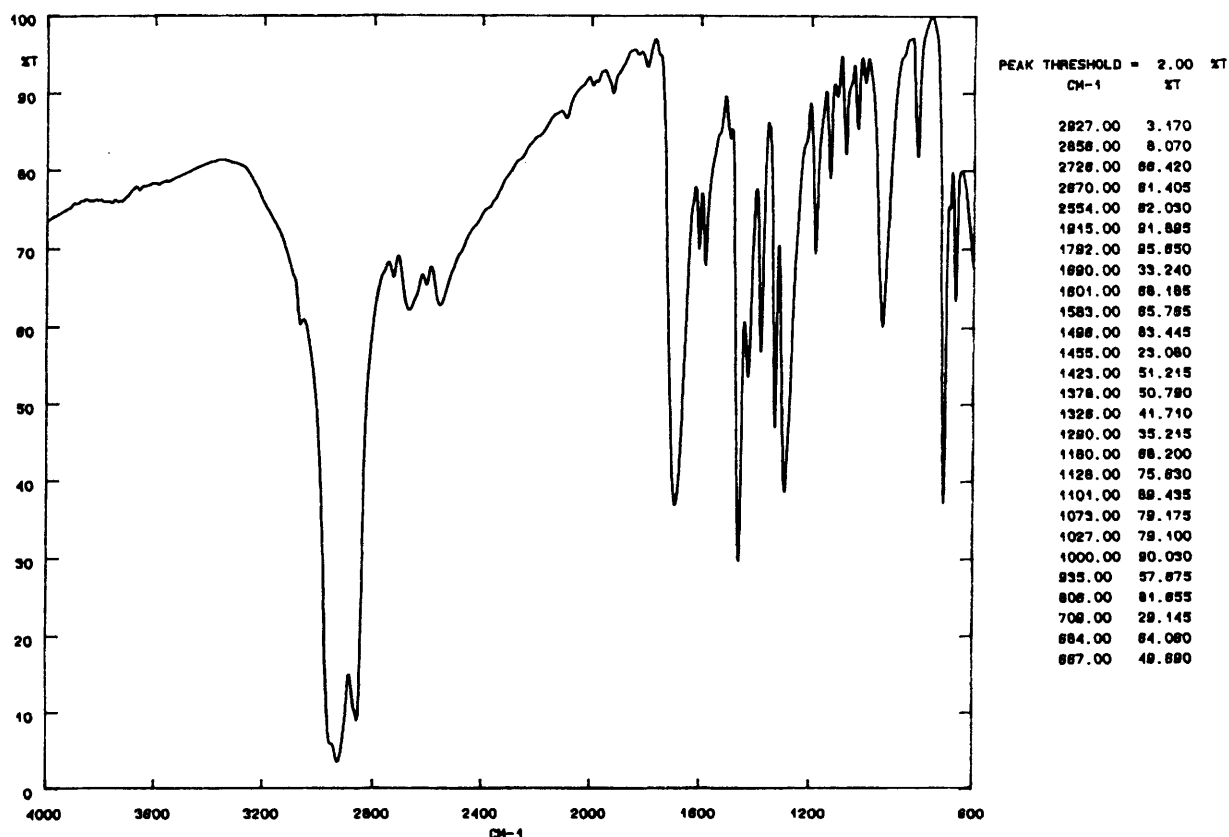


Figure 1.5

infrared spectrum an easy task. A typical carboxylic acid spectrum is that of benzoic acid,  $\text{PhCOOH}$ , which is shown in Figure 1.5.

As we move to lower frequencies in the infrared range, the next peak that we encounter is the C-H peak in the region  $3100\text{--}2700\text{ cm}^{-1}$ . This supplies little useful structural information since almost all organic compounds contain hydrogen, and in the case of a solid run as a mull it will certainly be present in the liquid hydrocarbon used to make the mull. After the C-H absorption, we leave the high-frequency high-intensity X-H bonds, and, after a usually blank region of the spectrum, encounter the weaker triple bond absorption frequencies. The most common are the C≡N bond, which absorbs at  $2300\text{--}2200\text{ cm}^{-1}$ , and the C≡C bond, which absorbs in the region from  $2250$  to  $2100\text{ cm}^{-1}$ . This latter bond is particularly weak if neither carbon atom is bonded to hydrogen. The carbonyl group occurs next, absorbing over the unusually wide range of  $1850\text{--}1640\text{ cm}^{-1}$ . However, the variation of the position of the C=O peak within this range is very valuable diagnostically, and will be considered separately.

As we further descend the frequency scale, we next come to the C=C bond region, which covers  $1680\text{--}1620\text{ cm}^{-1}$  in unconjugated systems, and can go as low as  $1590\text{ cm}^{-1}$  in conjugated systems. The C=C bond is often of low intensity, especially when fully substituted, and it is easily missed. In an aromatic system, the C-C bonds usually have two or three absorption peaks between approximately  $1600$  and  $1500\text{ cm}^{-1}$ , usually with the strongest peak at about  $1500\text{ cm}^{-1}$ . The spectrum of benzoic acid shown in Figure 1.5 illustrates this with weak peaks at  $1601\text{ cm}^{-1}$  and  $1583\text{ cm}^{-1}$ , and a stronger peak at  $1496\text{ cm}^{-1}$ .

The region below about  $1500\text{ cm}^{-1}$  is usually complex, and contains relatively little information about functional groups. It is often referred to as

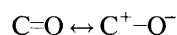
**Table 1.1** *Infrared absorption frequencies of common functional groups*

Functional group	Absorption range (cm <sup>-1</sup> )
N-H	3500–3250
CON-H	3500–3000
O-H	3700–3200
COO-H	3200–2200
C-H	3100–2700
C≡N	2300–2200
C≡C	2250–2100
C=O	1850–1640
C=C	1680–1590
Aromatic	1600–1500

the ‘fingerprint region’, since this is the region of greatest value when comparing the spectrum of an unknown compound with that of a known compound. At the lower frequency end of this region we come to the C-Cl bond absorption in the region 800–400 cm<sup>-1</sup>. The C-Br and C-I bonds usually absorb at too low a frequency for most spectrometers. The halogens are more readily identified by mass spectrometry.

The absorbing frequencies discussed above have been collected together in Table 1.1.

The carbonyl absorption was referred to earlier as covering a very wide range of frequencies. The absorption frequency is unusually sensitive to substitution at the carbonyl carbon atom. The reason for this is that the carbonyl group exists as a resonance hybrid of two forms:



The two forms absorb at different frequencies, the polar C<sup>+</sup>-O<sup>-</sup> having the higher frequency absorption. If we now consider the hybrid



it is easy to see that electron withdrawing substituents will favour the C<sup>+</sup>-O<sup>-</sup> form, and electron supplying substituents will favour the C=O form.

When the substituent X is a chlorine atom, this strongly electron withdrawing group favours the C<sup>+</sup>-O<sup>-</sup> bond, so acid chlorides absorb in the region around 1815–1790 cm<sup>-1</sup>. The carbonyl group is another electron withdrawing substituent, so that the anhydride absorbs in this region, but since we have two carbonyl groups close together we can have in-phase and out-of-phase vibrations, as with the NH<sub>2</sub> group. Saturated carboxylic acid anhydrides thus show two peaks, one in the region 1850–1800 cm<sup>-1</sup> and the other in the region 1790–1740 cm<sup>-1</sup>.

The position of the carbonyl peak, however, does not depend entirely on inductive effects. In esters, the overlap of the lone pair of electrons on X with the C=O bond reduces the double bond character of the C=O bond, so the ester carbonyl group absorbs in the range 1755–1735 cm<sup>-1</sup>. Aldehydes and ketones come next at 1740–1700 cm<sup>-1</sup>, then the carboxylic acid carbonyl absorbs at 1725–1700 cm<sup>-1</sup>, which is lower than might have been expected, but its position is affected by the dimeric nature of the carboxylic acid group in solution.

All these examples have referred to the carbonyl carbon atom attached to a



**Table 1.2** Infrared absorption frequencies of substituted carbonyl groups

Functional group	Absorption frequency range ( $\text{cm}^{-1}$ )	
	<i>R</i> = Aliphatic	<i>R</i> = Conjugated alkene or aromatic
Anhydride, $\text{RCOOCOR}$	1850–1800 and 1790–1740	1830–1775 and 1770–1710
Acid chloride, $\text{RCOCl}$	1815–1790	1790–1750
Ester, $\text{RCOOR}^*$	1800–1745	
Ester, $\text{RCOOAlkyl}$	1755–1730	1735–1710
Aldehyde, $\text{RCOH}$	1740–1715	1715–1680
Ketone, $\text{RCOAlkyl}$	1725–1700	1700–1665
Carboxylic acid, $\text{RCOOH}$	1725–1700	1715–1680
Amide, $\text{RCON}$	1680–1640	1695–1665

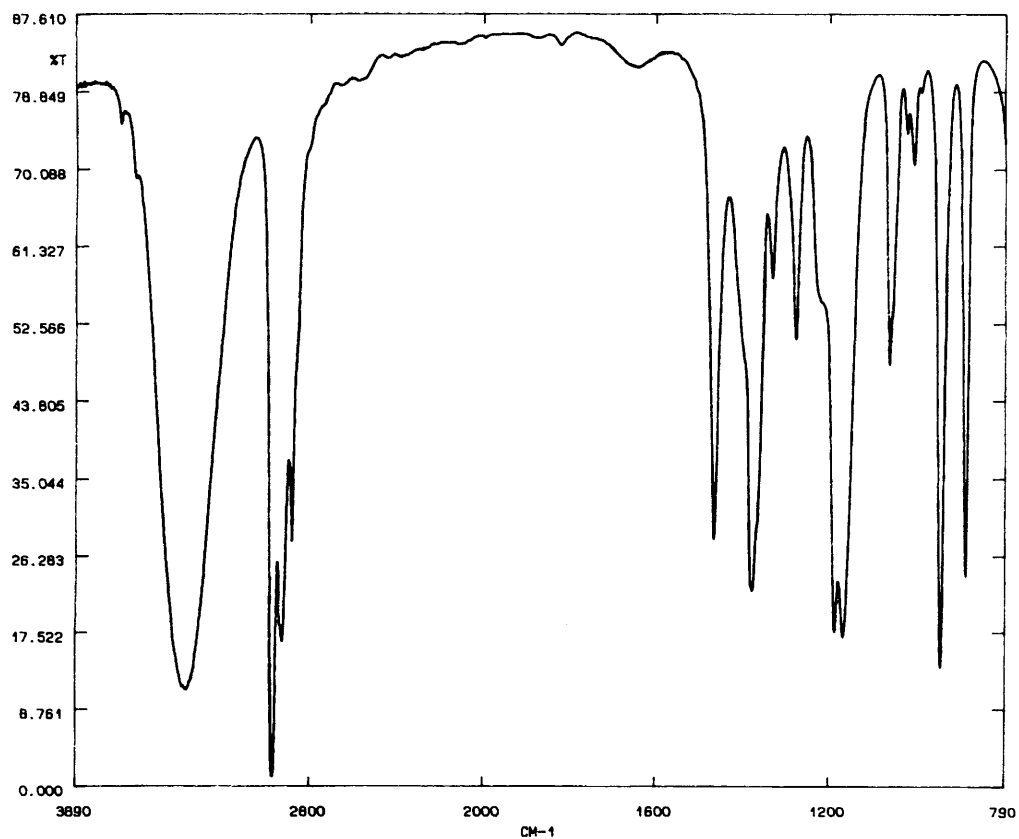
\**R* = aryl or vinyl.

saturated group; if it is attached to a multiple bond or an aromatic ring, then the carbonyl absorption frequency is lowered by  $15\text{--}40\text{ cm}^{-1}$ . Thus, if we need to assign a carbonyl group, it is first necessary to see if the molecule shows signs of unsaturation; if this is next to the carbonyl carbon atom, then carbonyl frequencies will be lower than expected. Unexpectedly, conjugation shifts the amide carbonyl to higher frequency. It may be due to an inductive effect on the conjugated  $\text{CO-N}$  system.

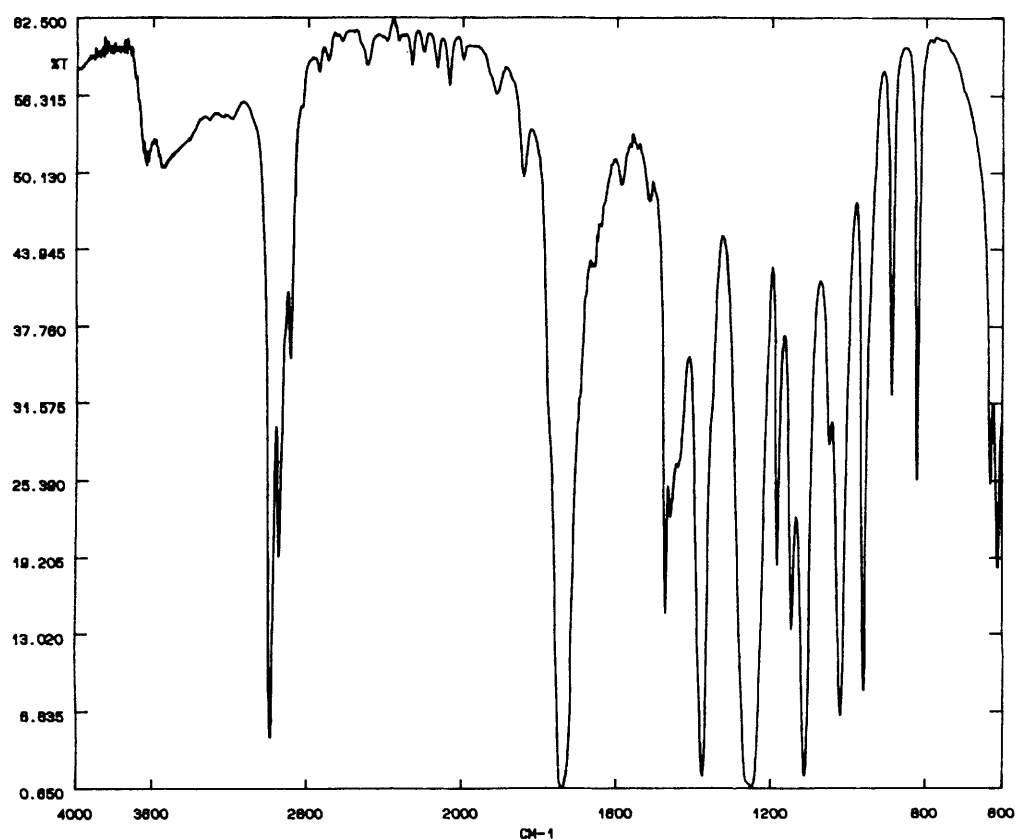
The carbonyl absorption frequencies have been collected together in Table 1.2.

### Problems in Interpreting Infrared Spectra

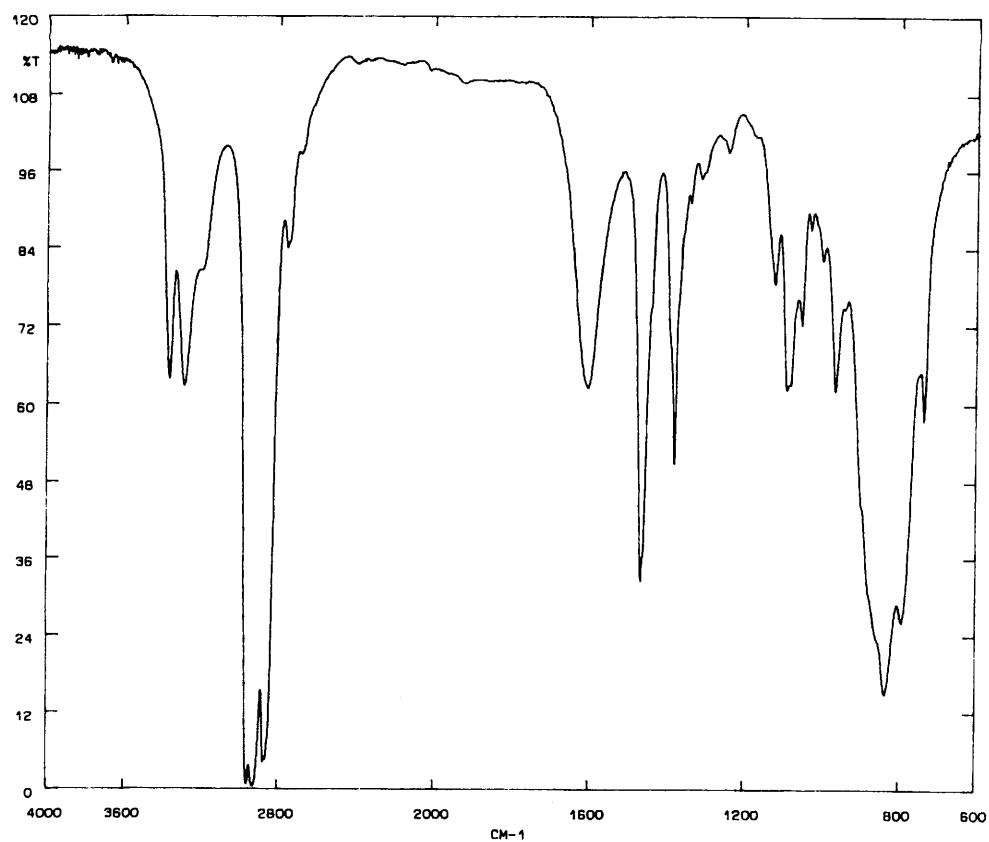
Using the data given in Tables 1.1 and 1.2, you should now be able to identify the common functional groups present in the compounds whose spectra comprise Samples 1 to 20. Remember that it is not sufficient to identify a compound as simply a carbonyl compound. If you observe a carbonyl peak, you should check for the presence of an aromatic ring or a double bond in the molecule, then use the data in Table 1.2 to say what type of carbonyl group (*e.g.* anhydride, ketone) is present in the sample. Note that some spectra are consistent with more than one structural type, since ranges of frequencies can overlap. All the spectra are run on pure liquids or nujol mulls.



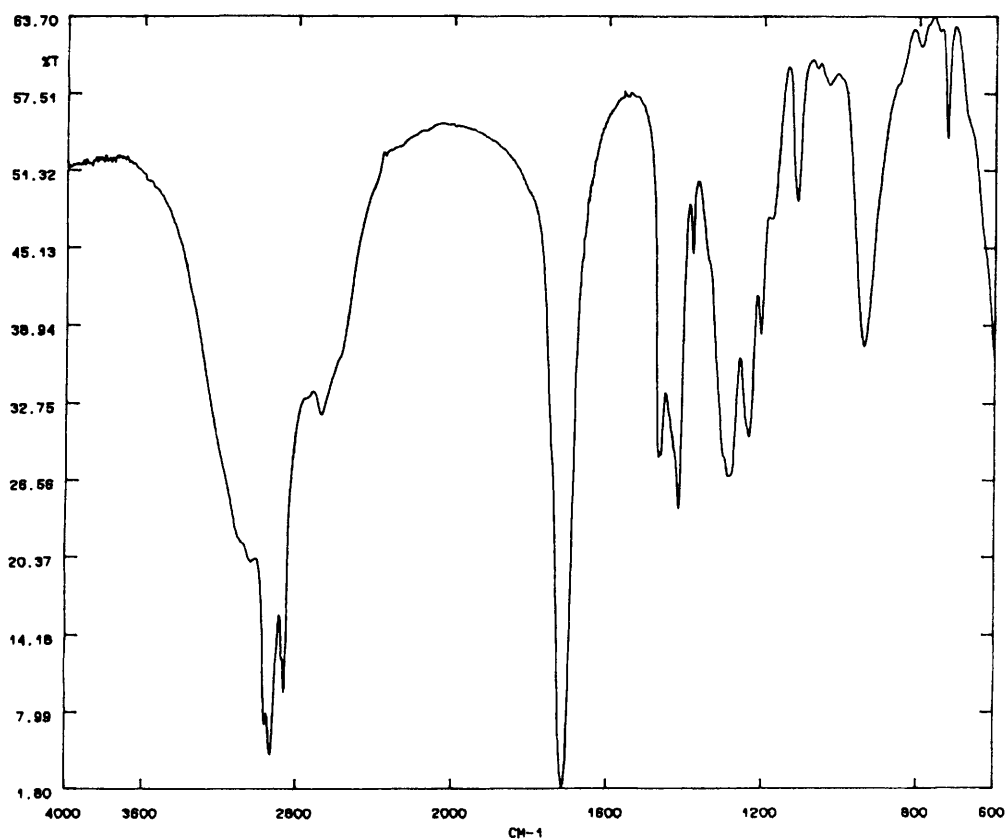
Sample 1.1



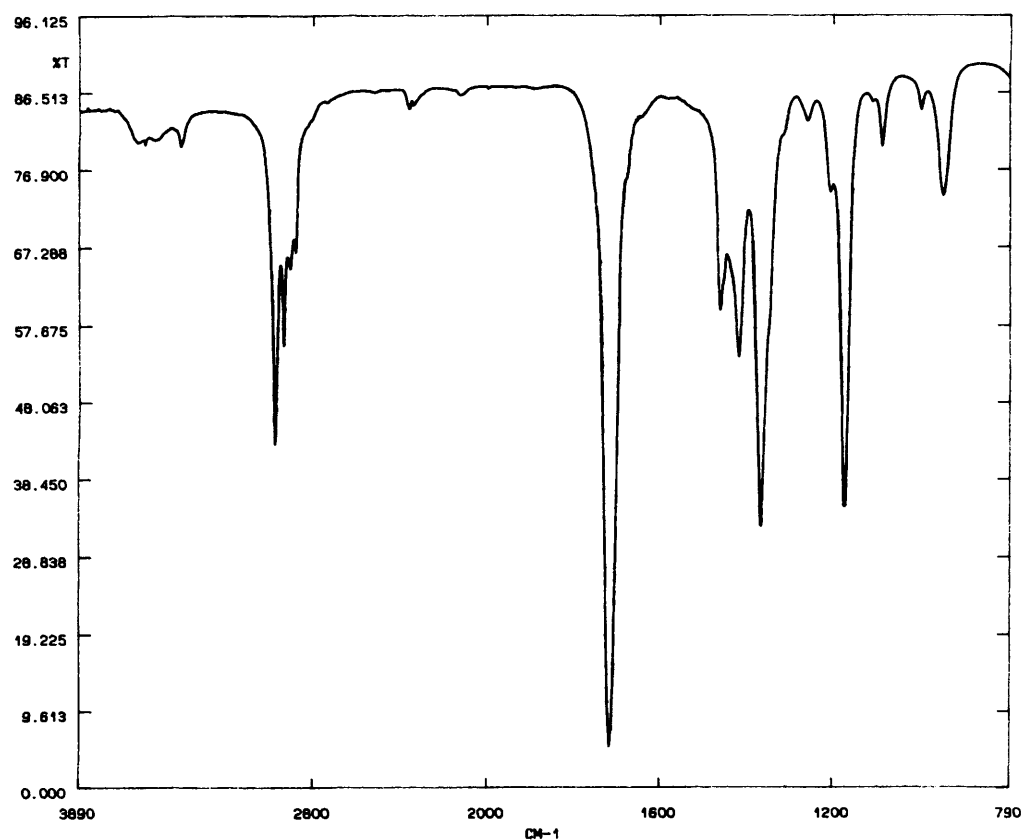
Sample 1.2



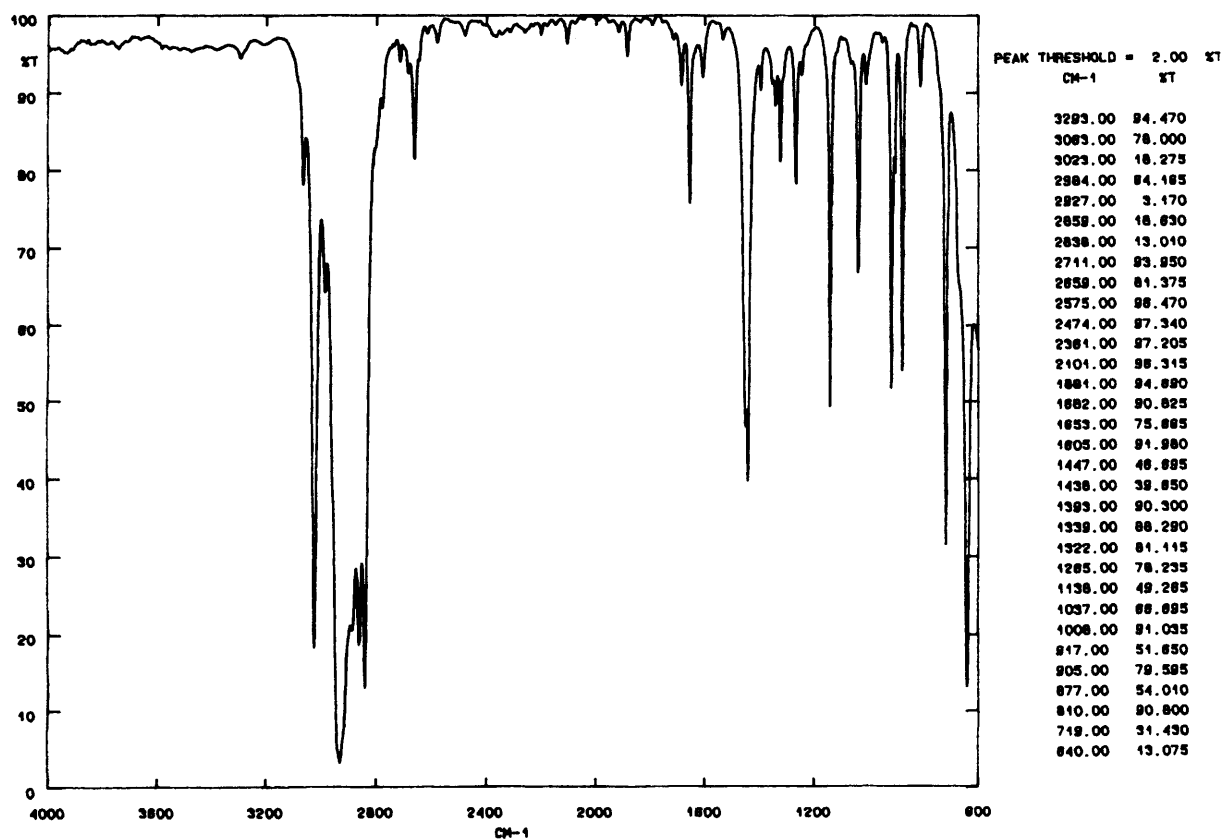
Sample 1.3



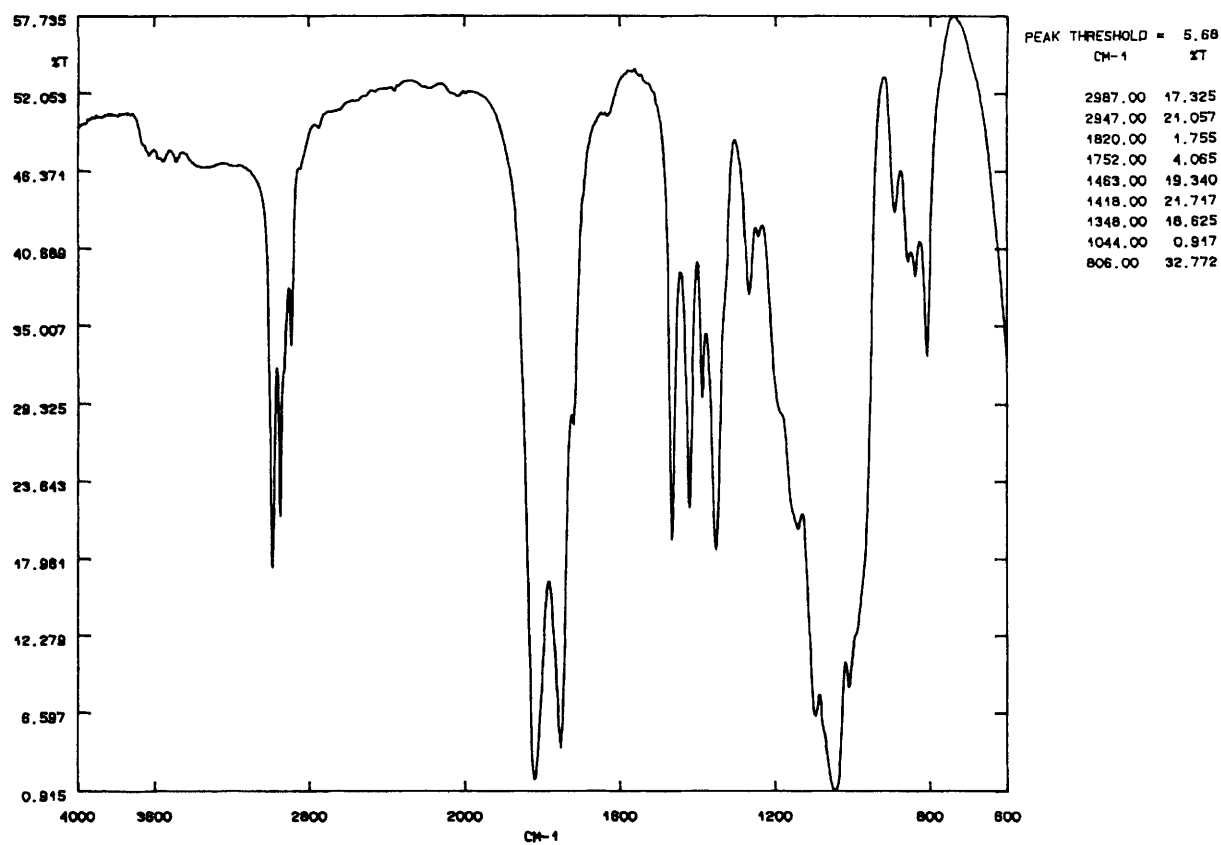
Sample 1.4



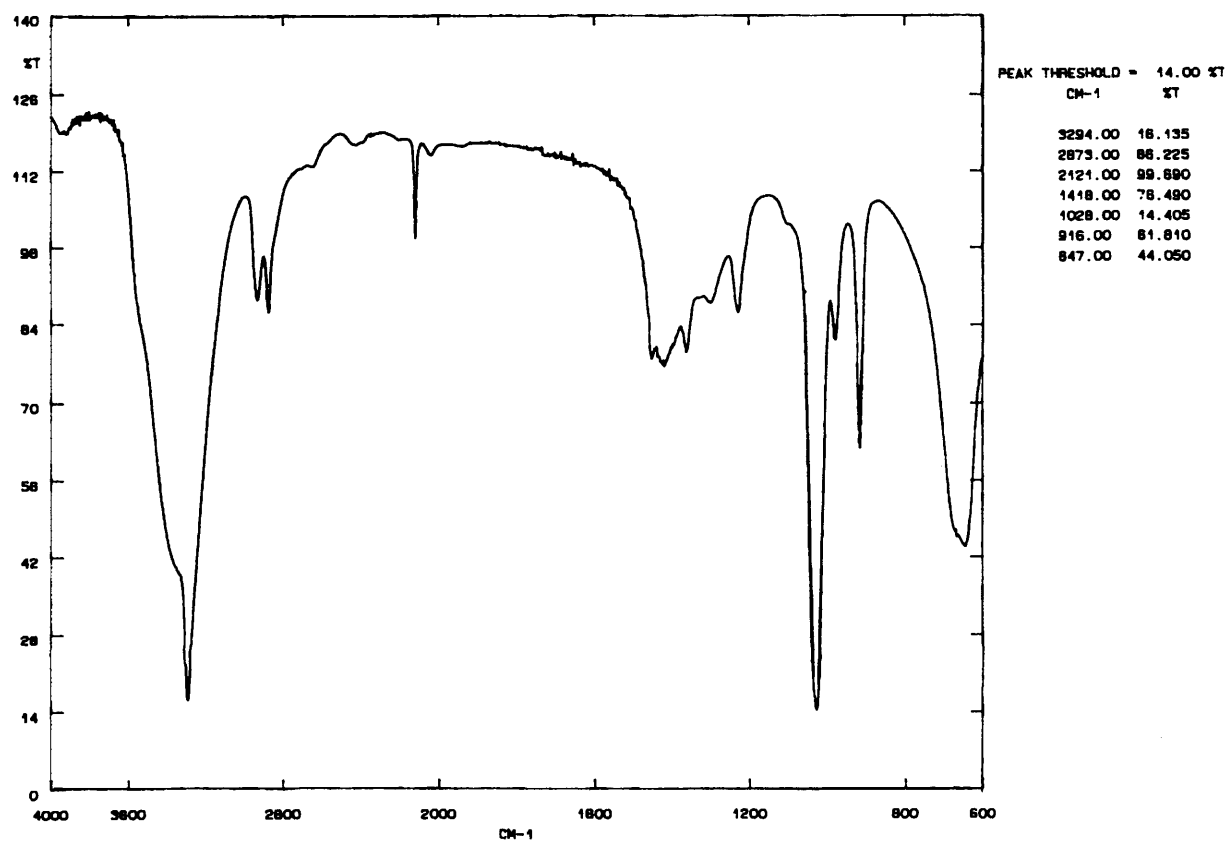
Sample 1.5



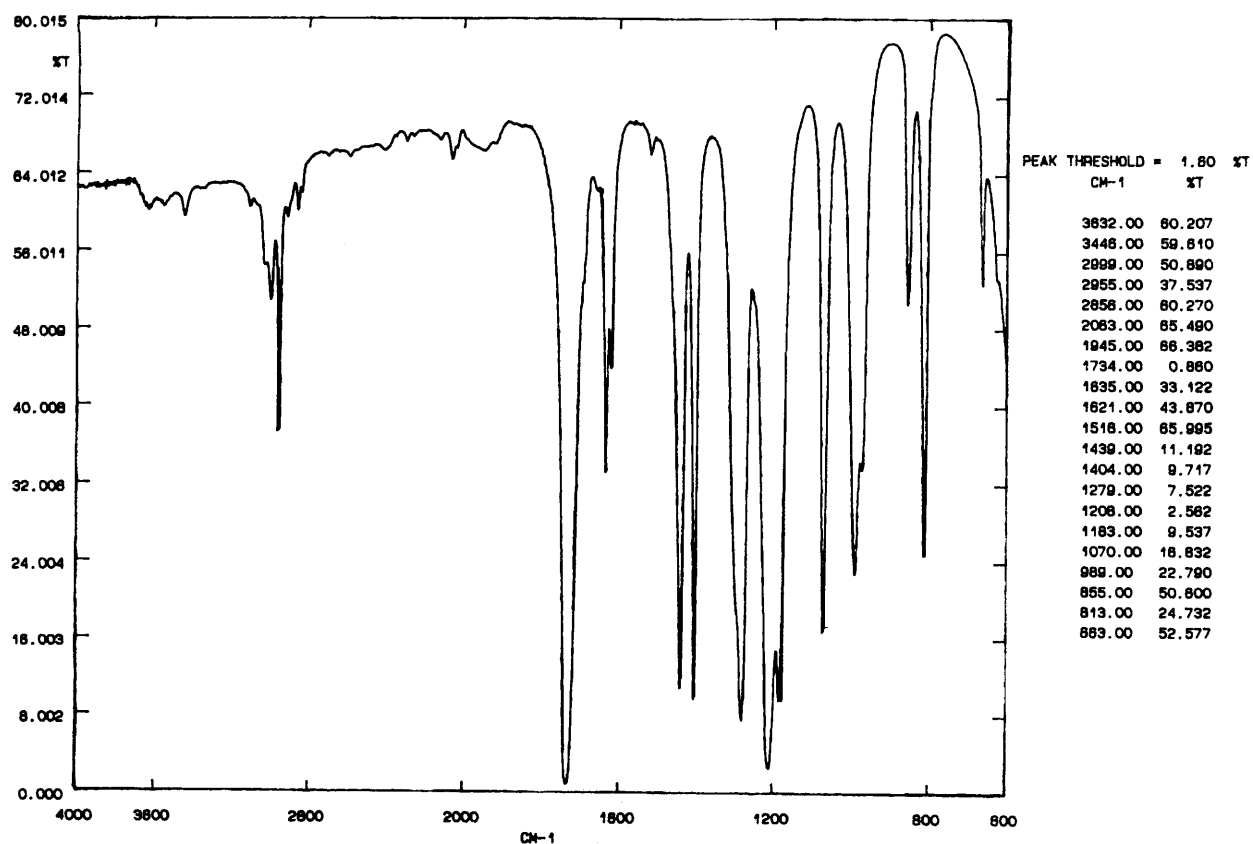
Sample 1.6



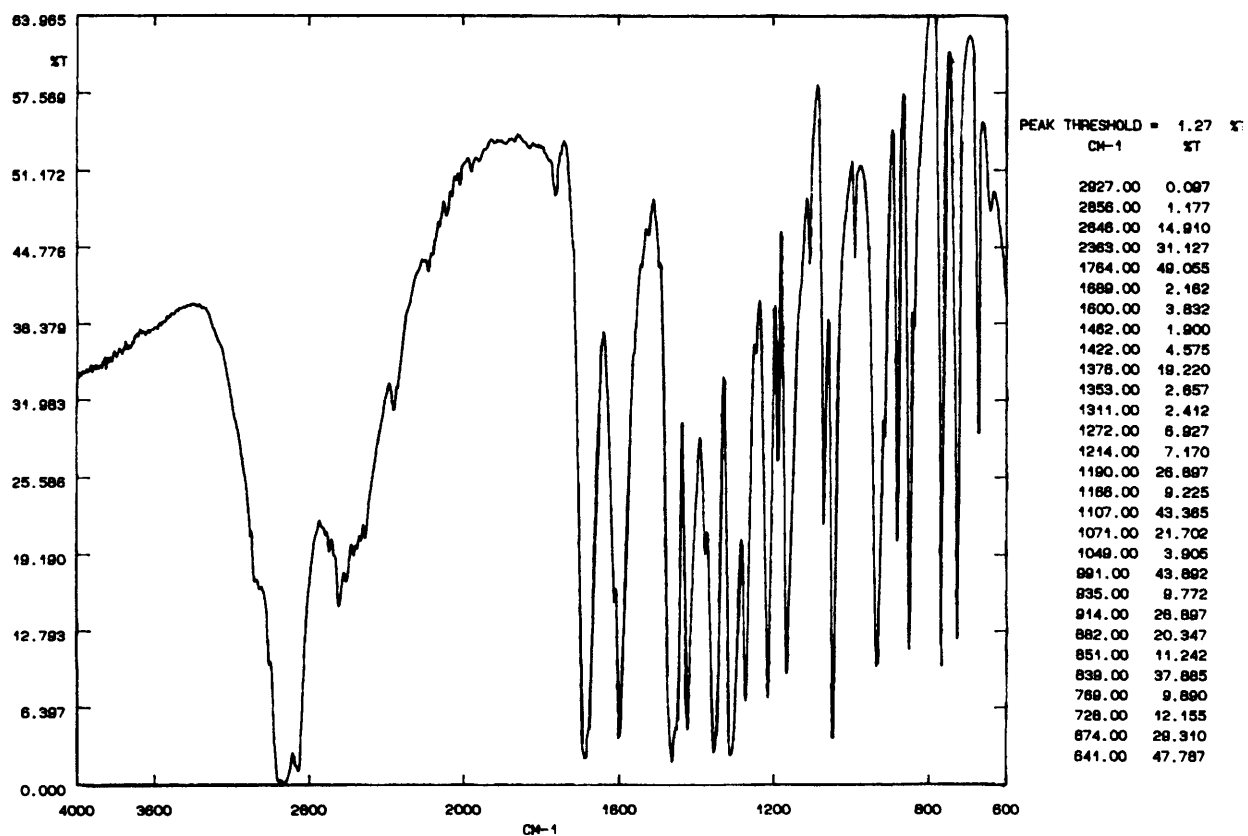
Sample 1.7



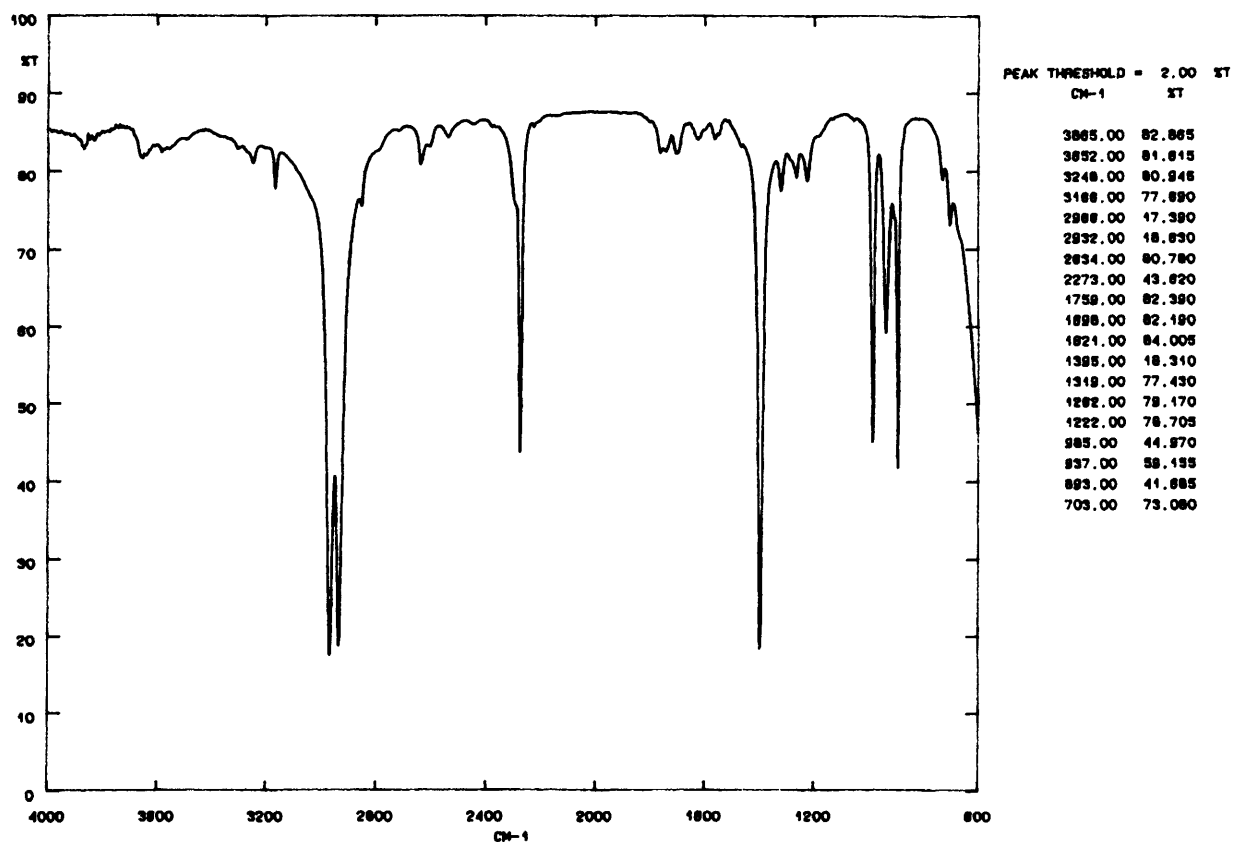
Sample 1.8



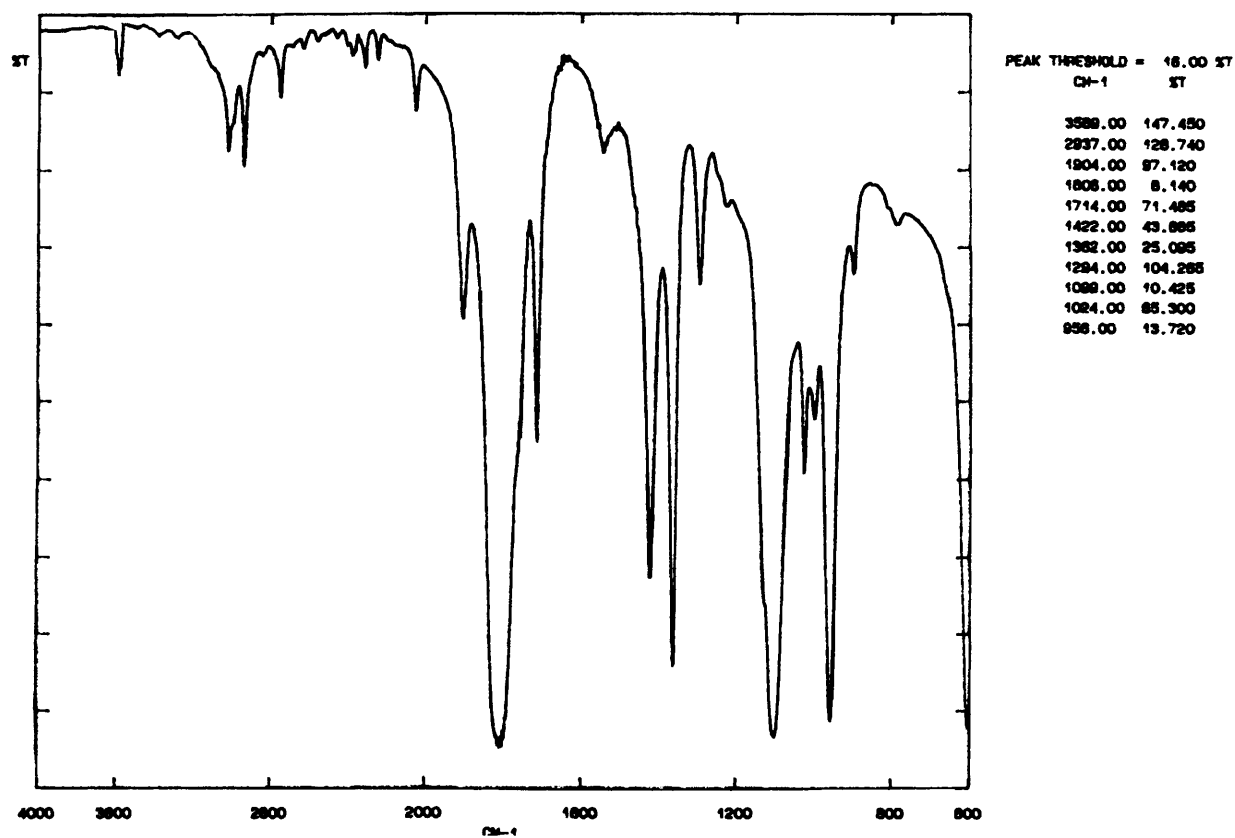
Sample 1.9



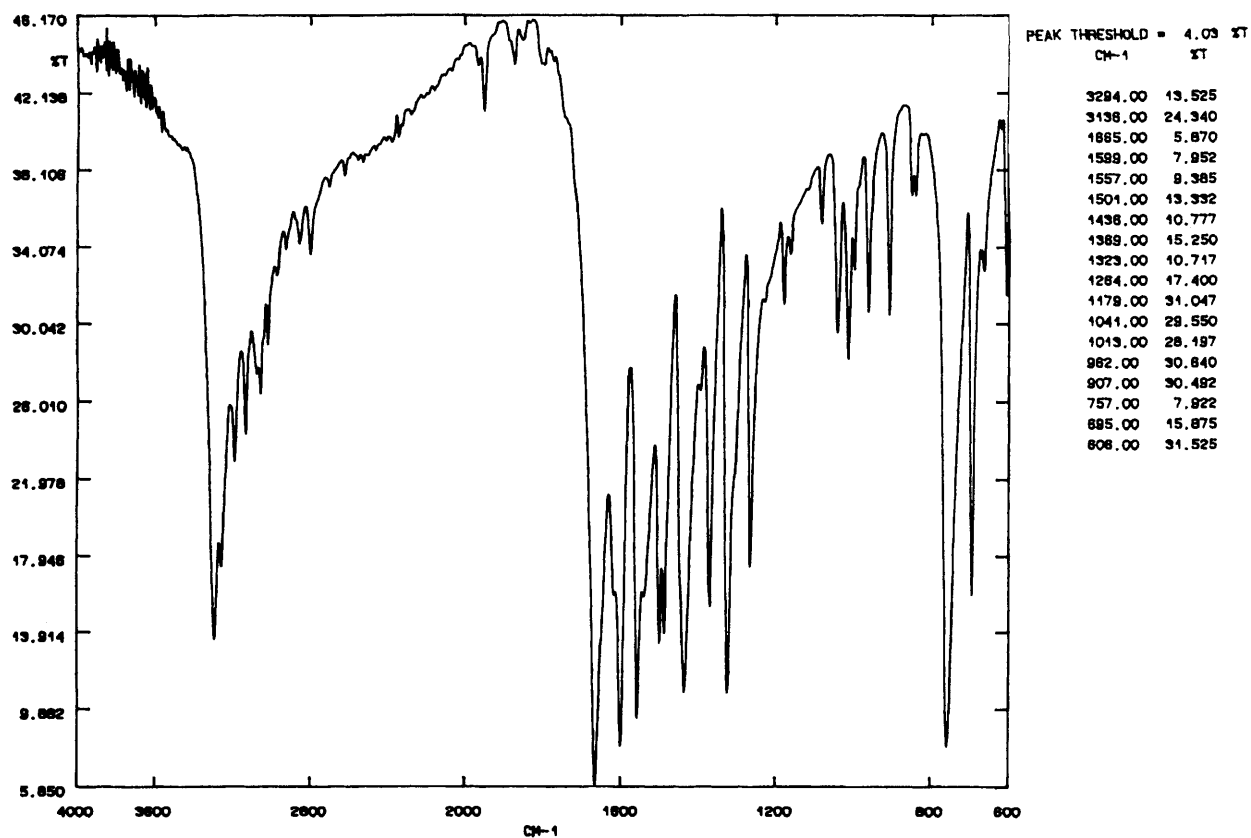
Sample 1.10



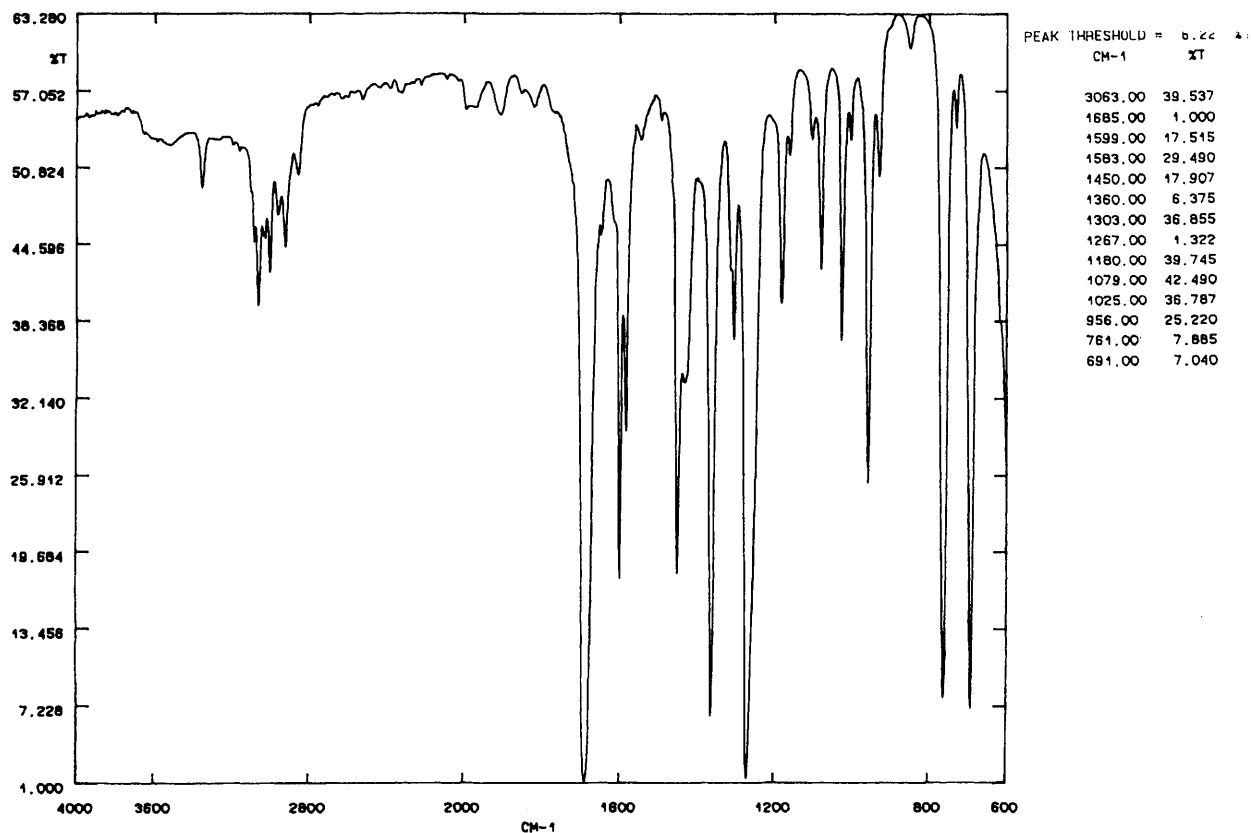
Sample 1.11



Sample 1.12

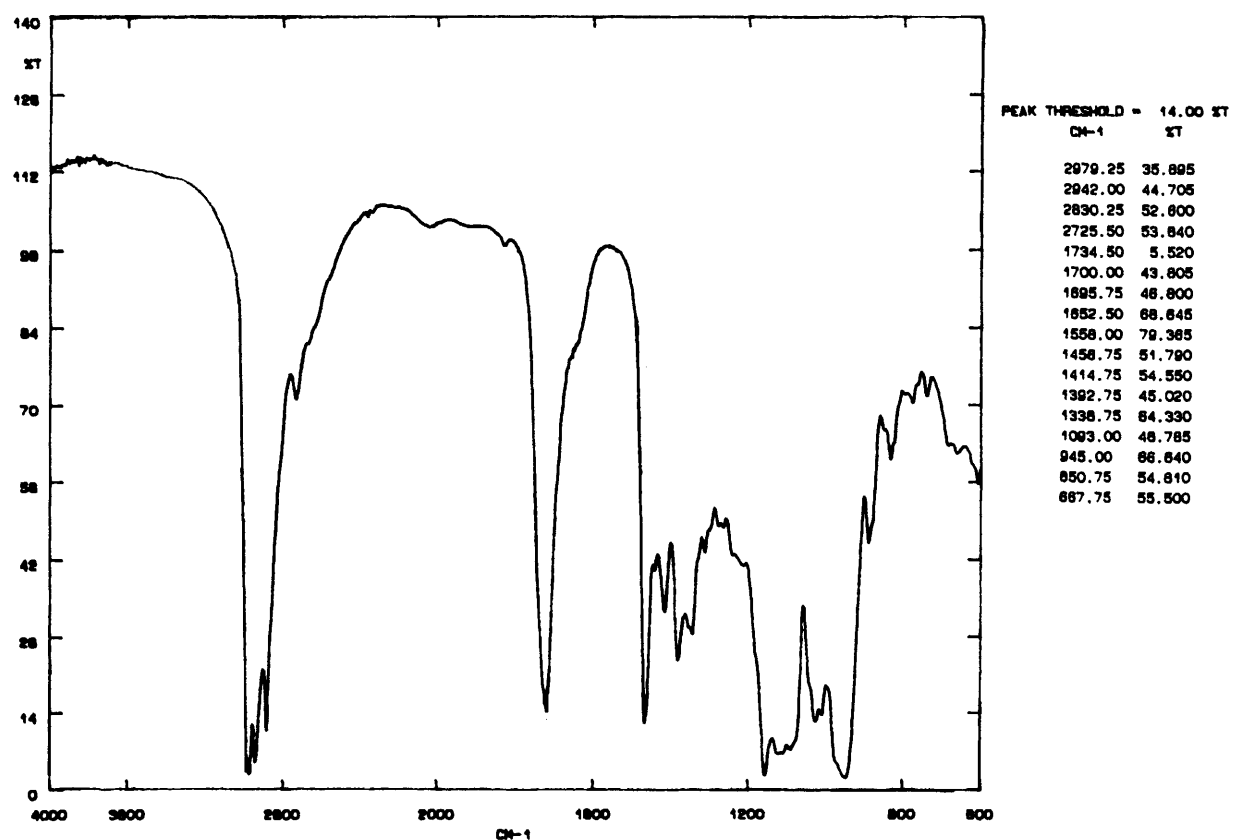


Sample 1.13

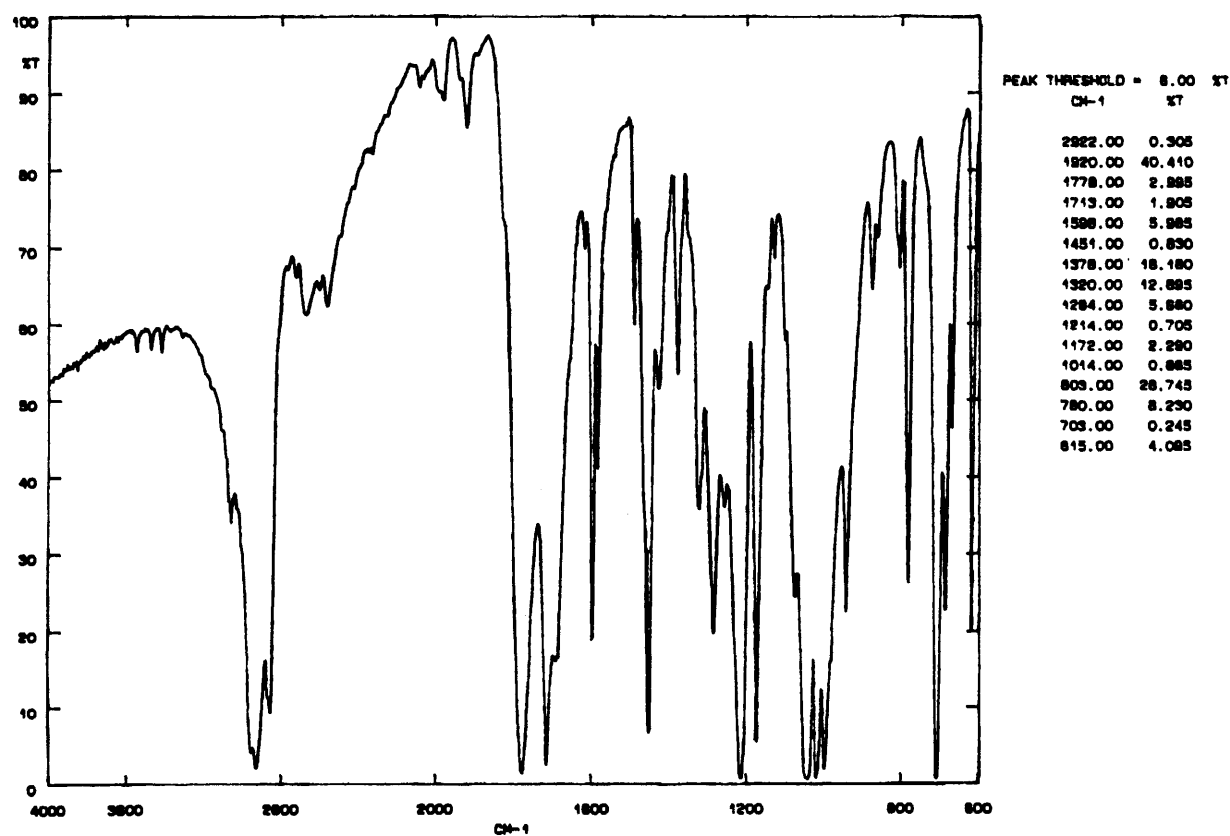


Sample 1.14

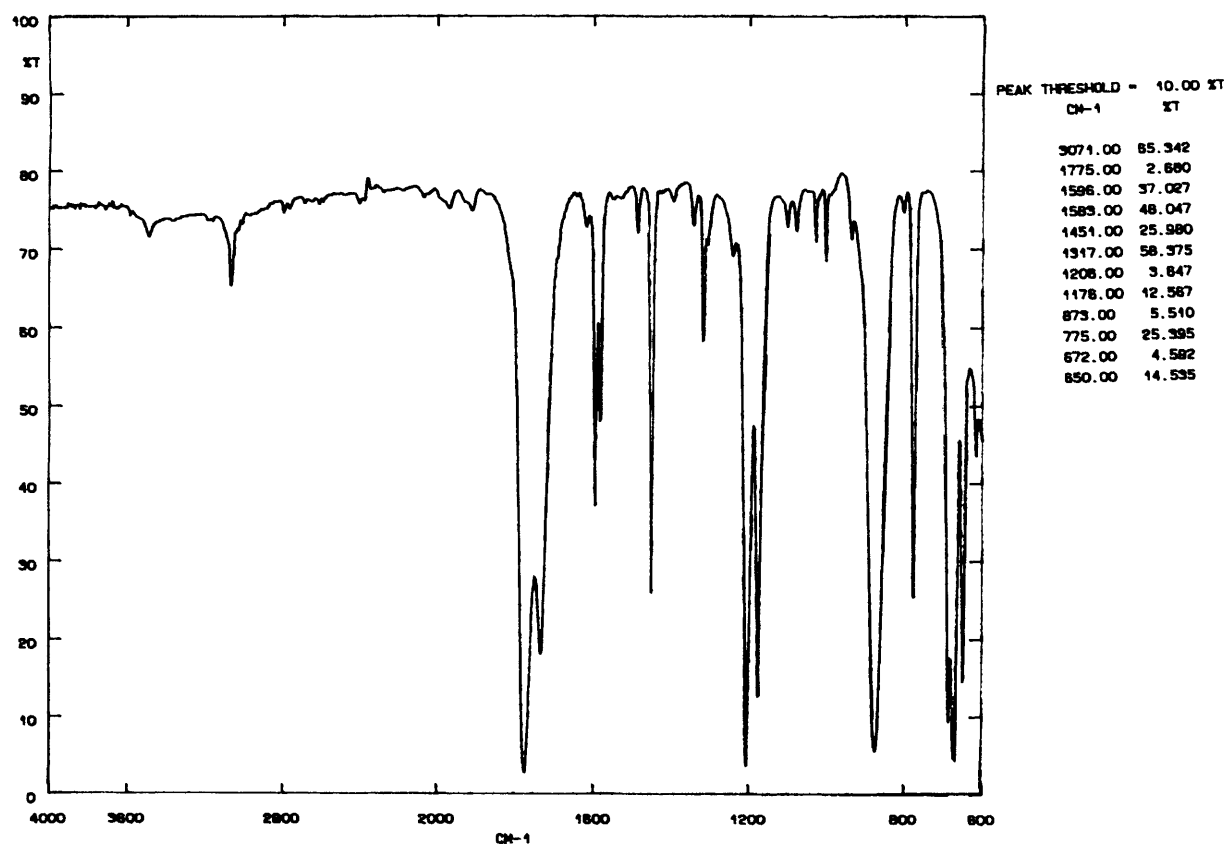




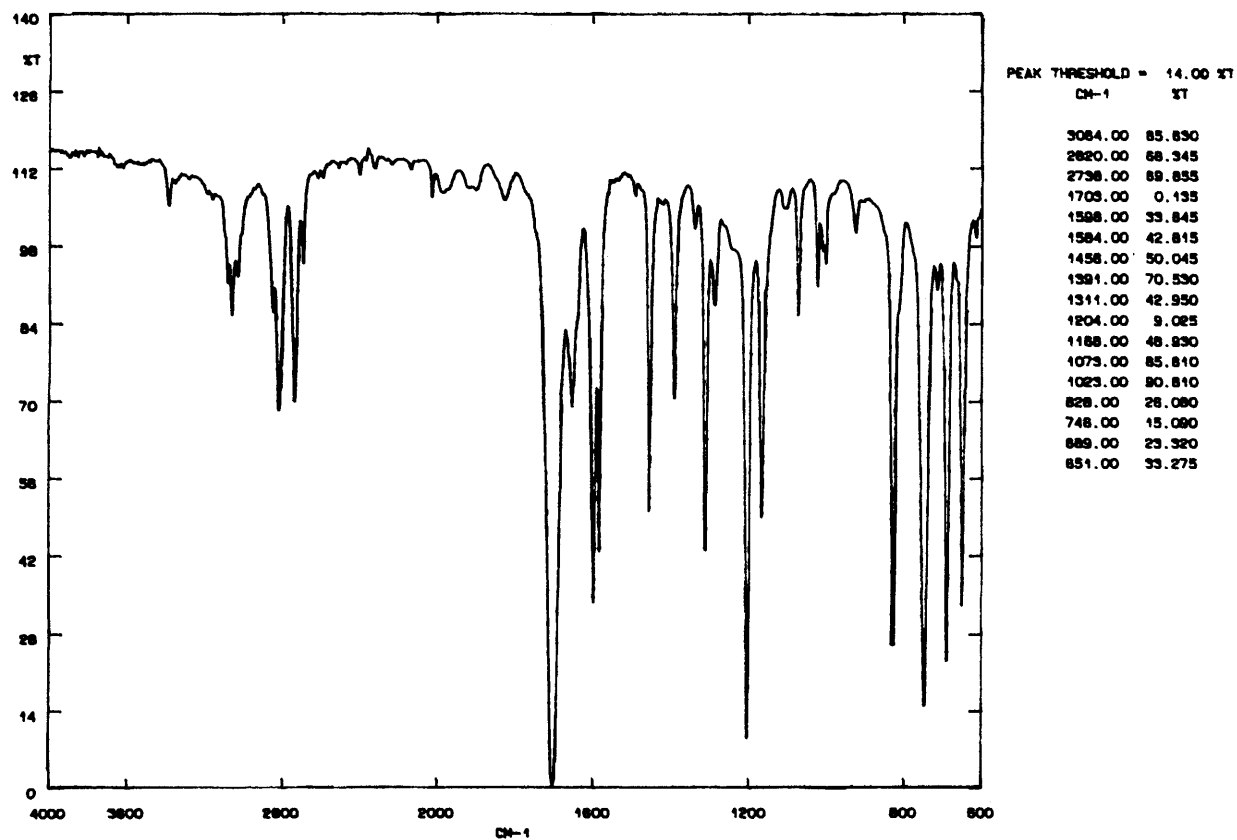
Sample 1.15



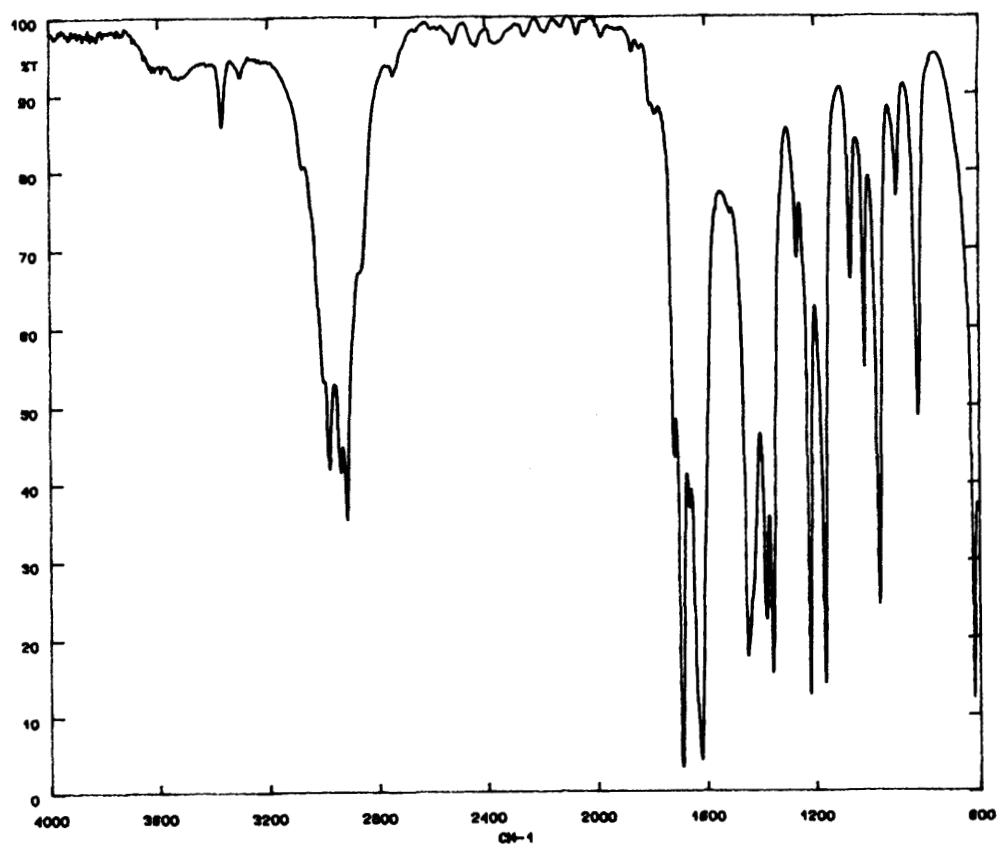
Sample 1.16



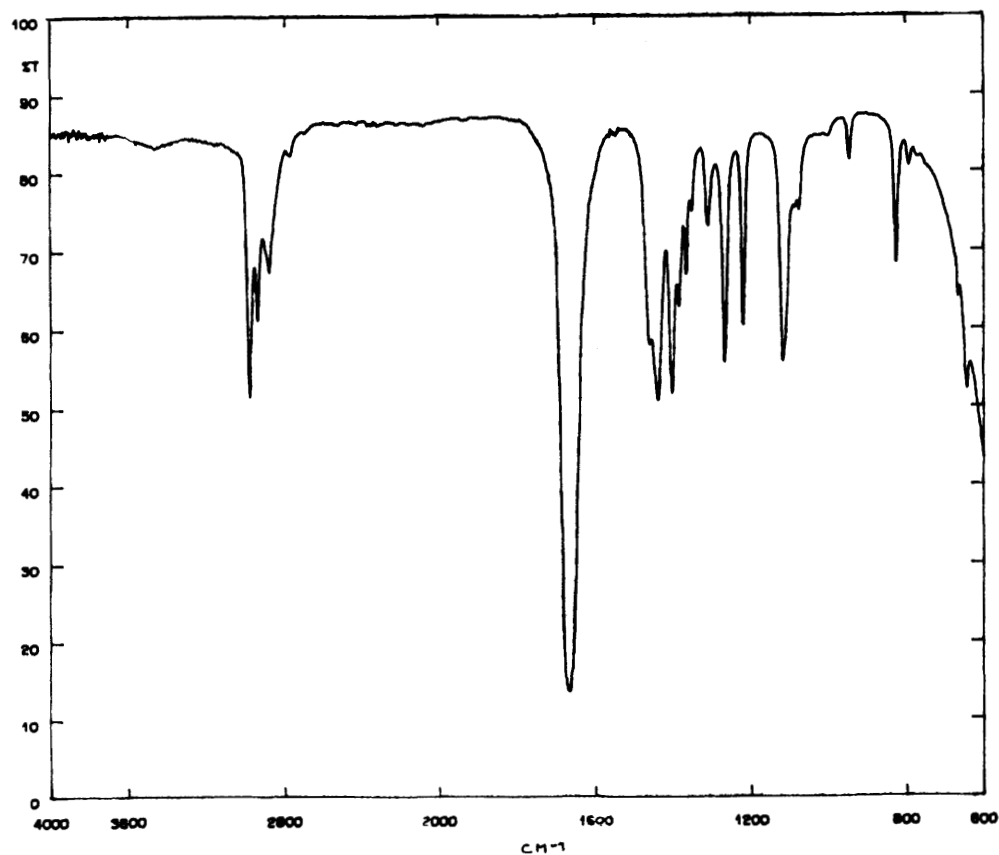
Sample 1.17



Sample 1.18



Sample 1.19



Sample 1.20



## Mass Spectrometry

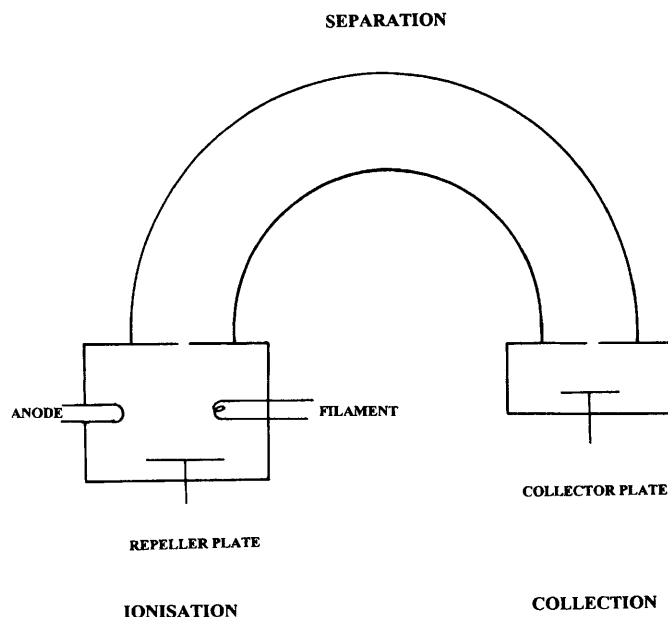
Mass spectrometry gives us some information about the structure of a molecule. It can usually tell us the molecular weight of a substance, and can detect the presence of bromine, chlorine and iodine. It may be possible to deduce the structure of a compound from its mass spectrum.

Unlike the other techniques studied in this book, it is a spectrometric, not a spectroscopic, method. It does not involve the absorption of radiation; it consists of generating ions of such energy that they fragment, collecting fragments of the same mass together, and weighing them. Some fragments are more stable than others, and so are produced to a much greater extent than others, and we see large peaks in the spectrum at their mass. Using knowledge of favoured fragmentations, a surprising amount of information about the structure of the original molecule can be obtained.

Mass spectrometers operate at very low pressures, so that the ions can travel long distances without undergoing collisions. The mass spectrometer consists basically of three parts, as shown schematically in Diagram 2.1. The regions of the spectrometer can be described according to their function, as ionisation, separation and collection.

### Ionisation

The material to be studied is introduced into the ionisation chamber in the vapour phase. It is bombarded with a stream of electrons, generated by the filament and accelerated to about 70 eV by the anode.



**Diagram 2.1** Schematic diagram of a mass spectrometer

If an electron at this energy hits one of the atoms being studied, the atom gains considerable vibrational energy, causing it to ionise and usually fragment. The ions produced pass through a series of slits into the analysing system.

This method of ionisation is used for most samples which are reasonably stable and reasonably volatile. A number of other ionisation methods exist to tackle less stable or less volatile samples, but all work on the same principle: the molecule absorbs energy and breaks down to its more stable ions.

### Ion separation

Ionisation of a compound gives a series of ions of different masses, but almost all carry a single positive charge. The stream of positive ions needs to be separated according to the mass to charge ratio, usually denoted by  $m/z$ , which effectively separates them by mass, as  $z = 1$ . This is done by passing the beam through a magnetic field, which deflects lighter ions more than heavier ions. The actual amount of deflection is dependent on the mass to charge ratio,  $m/z$ . At the end of the travel through the magnetic field, the beam passes through a narrow slit, and proceeds to the collector. By varying the magnetic field, ions of any  $m/z$  ratio can be focused on the collector slit, and the spectrum scanned.

Most mass spectrometers use a more complex arrangement of electrostatic and magnetic analysers in order to improve the resolution of the instrument, but the principle involved is the same.

### Ion collection

When the ions reach the collector, ions of each  $m/z$  ratio land on the collector plate for a similar interval of time, and build up a charge which is amplified and recorded.

One of the great advantages of mass spectrometry is that it can work with extremely small samples, less than  $10^{-12}$  of a mole. It is often used coupled to a gas-liquid chromatography analyser, and the separated fractions are run automatically into the mass spectrometer. It is particularly valuable for the study of biological samples.

The mass spectrometer ionises the molecules, then divides the ions up according to their  $m/z$  ratio, and measures the amount of ions of each  $m/z$  ratio. The result is presented as a bar chart, as shown in Figure 2.1, the mass spectrum of *n*-octane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ .

Along the base of the chart, the scale is in  $m/z$  ratio values, but since  $z = 1$ , these can be regarded as the masses of the ions. The vertical scale shows the amount of each ion. Since the amount of any ion collected obviously depends on how long the collector plate has been in the ion beam, we adopt an arbitrary scale for intensity, in which the largest peak is given an intensity value of 100 and is known as the parent peak. All other peaks have their intensities measured as a percentage of the parent peak.

Before we start to look at the structural information which can be obtained, we need to consider the information which can be obtained from isotope masses and ratios. One of the most useful things we can do is to measure the accurate mass of a peak. The atomic weights of most isotopes are not quite integral numbers, and most have been measured accurately to six places of decimals. A few useful accurate masses are given in Table 2.1.

If we measure the molecular weight of any ion to six-figure accuracy, on the basis of that molecular weight we can assign a unique chemical composition to

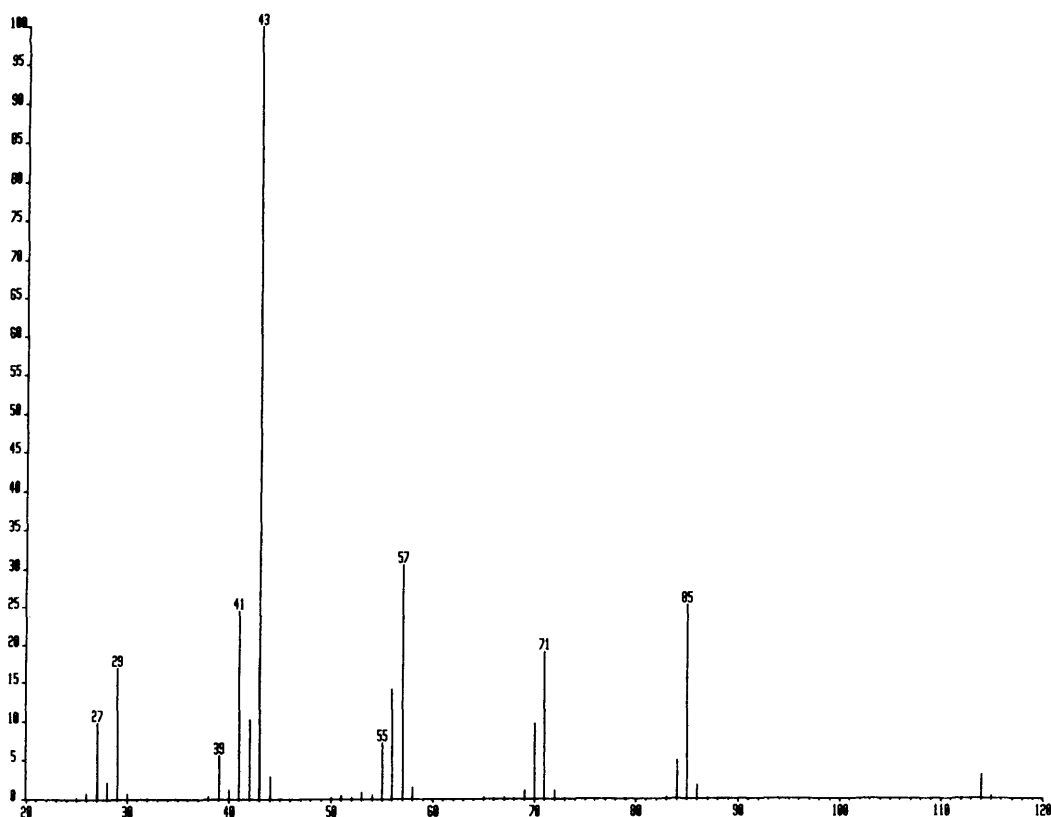


Figure 2.1

**Table 2.1** *Accurate atomic weights of some common isotopes*

<i>Isotope</i>	<i>Atomic weight</i>
$^1\text{H}$	1.007825
$^{12}\text{C}$	12.000000
$^{14}\text{N}$	14.003074
$^{16}\text{O}$	15.994915
$^{35}\text{Cl}$	34.968855
$^{79}\text{Br}$	78.918348
$^{127}\text{I}$	126.904352

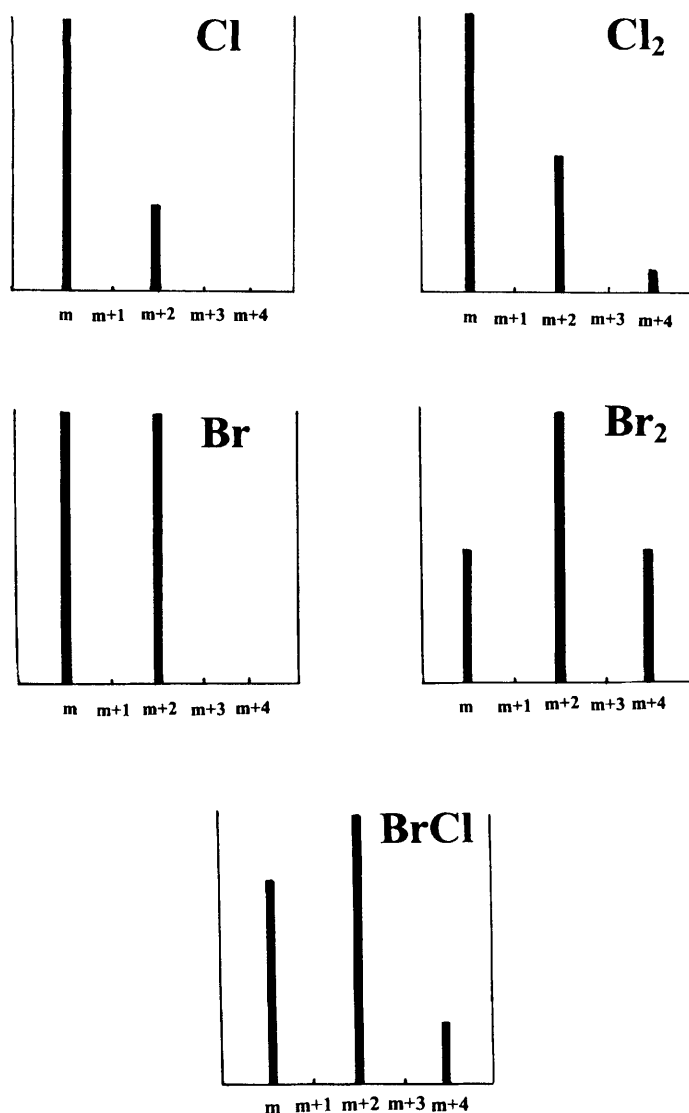
that ion. As an example, assume we have an ion of  $m/z$  ratio 28. The composition of this ion could be  $\text{N}_2$ ,  $\text{C}_2\text{H}_4$  or  $\text{CO}$ . If we calculate the exact weights of these ions, we find they differ significantly:

- $^{14}\text{N}_2$  has molecular weight 28.006148
- $^{12}\text{C}_2^{1}\text{H}_4$  has molecular weight 28.031300
- $^{12}\text{C}^{16}\text{O}$  has molecular weight 27.994915

Thus, we can identify the peak of  $m/z$  28 by measuring its accurate mass. We do not have to worry about the isotopic composition of C, N or H, as the presence of  $^2\text{H}$ ,  $^{15}\text{N}$  or  $^{13}\text{C}$  would result in a separate peak of  $m/z$  greater than 28.

The method requires a larger sample than can be provided by gas chromatography–mass spectrometry (GC/MS), and is time consuming, but it remains a valuable approach to the determination of molecular composition.

We saw that in order to define the composition of the ion, we had to specify its isotopic as well as its chemical composition. Some elements exist as



**Diagram 2.2** Mass spectrum peak patterns of ions containing chlorine and bromine

mixtures of isotopes in which appreciable amounts of each isotope are present, and then we always get a mixture of ions of different isotopic composition. Since chlorine has two isotopes,  $^{35}\text{Cl}$  with an abundance of 75.8% and  $^{37}\text{Cl}$  with an abundance of 24.2%, then an ion containing chlorine will always have two peaks, separated by two mass units, in the ratio of approximately 3 to 1. Similarly, bromine consists of 50.5% of  $^{79}\text{Br}$  and 49.5% of  $^{81}\text{Br}$ , so ions containing bromine always consist of a pair of peaks of equal size, separated by two mass units. The patterns produced, together with those resulting from  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{BrCl}$ , are shown in Diagram 2.2. Detection of these patterns is valuable evidence for the presence of chlorine or bromine in a molecule, especially as these elements are difficult to detect by infrared spectroscopy. Iodine exists as a single isotope, but has an atomic weight of 127, so it shows up very clearly in a mass spectrum.

Most other isotope compositions favour one isotopic species, but even these can give rise to significant extra peaks. Carbon is a mixture of 98.9%  $^{12}\text{C}$  and 1.1%  $^{13}\text{C}$ , so that a compound containing one carbon atom per molecule would have peaks in the ratio 98.9 to 1.1. However, if an ion has ten carbon atoms, we have ten chances of a  $^{13}\text{C}$  atom occurring in the ion, and the ion would have two peaks in the ratio of 89 to 11. Any sizeable peak in a mass



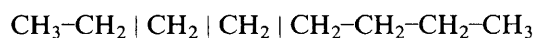
spectrum of an organic compound is thus likely to be followed by a peak 1 mass unit larger, whose size depends on the number of carbon atoms in the ion.

We can now return to the spectrum of *n*-octane, shown in Figure 2.1. The first thing to look for when we study a mass spectrum is the molecular ion, which gives us the molecular weight. In this case, it is the rather small peak at  $m/z$  114. One of the problems of mass spectrometry is identifying the molecular ion; in molecules containing only C, H, O and halogens, it is useful to note that the main peaks have odd  $m/z$  ratios, while the molecular ion has an even  $m/z$  ratio. If the molecule contains an odd number of nitrogen atoms this is reversed: the molecular ion has an odd  $m/z$  ratio, and most of the peaks have even  $m/z$  ratios. Having identified the molecular ion, we look at the differences in  $m/z$  ratios between the molecular ion and the main peaks in the spectrum, which gives us the number of mass units (known as Daltons) lost in each fragmentation. In the case of octane, these are:

Molecular ion		Ion		Mass lost	Possible fragment
114	–	85	=	29	$C_2H_5$
114	–	71	=	43	$C_3H_7$
114	–	57	=	57	$C_4H_9$
114	–	43	=	71	$C_5H_{11}$

We can then look at the most probable compositions of the fragments lost. In this case, we know that the molecule is octane, so can ignore possible compositions which contain oxygen. Even if we did not know this, we could say that the fragment of mass 43 Daltons which was lost cannot be  $CH_3CO$ , since that structural unit would also split next to the C–O linkage (see page 26), losing  $CH_3$  with a mass of 15 Daltons. A list of possible compositions of fragment ions is given in Table 2.2.

Our octane molecule thus has three main fragmentations:



Knowing that the molecule can split off  $C_2H_5$ ,  $C_3H_7$  or  $C_4H_9$  and has a molecular weight of 114 provides good evidence for the structure of *n*-octane; loss of fragments which increase in mass by 14 (*i.e.*  $CH_2$ ) is characteristic of an unbranched hydrocarbon chain. Note that octane does not readily lose  $CH_3$ . The fission of this species is energetically unfavourable, unless the residual ion is stabilised by an electron rich atom or group.

**Table 2.2** Possible losses from molecular ions

Mass lost	Possible group lost	Inference
15	$CH_3$	
17	OH	Alcohol
18	$H_2O$	Alcohol
29	$C_2H_5$ or CHO	–
31	$OCH_3$	Methyl ester
41	$C_3H_5$	Propyl ester
43	$C_3H_7$ or $CH_3CO$	–
44	$CO_2$	Anhydride
45	COOH	Carboxylic acid
	$OC_2H_5$	Ethyl ester
55	$C_4H_7$	Butyl ester
57	$C_4H_9$ or $C_2H_5CO$	–
71	$C_5H_{11}$ or $C_3H_7CO$	–

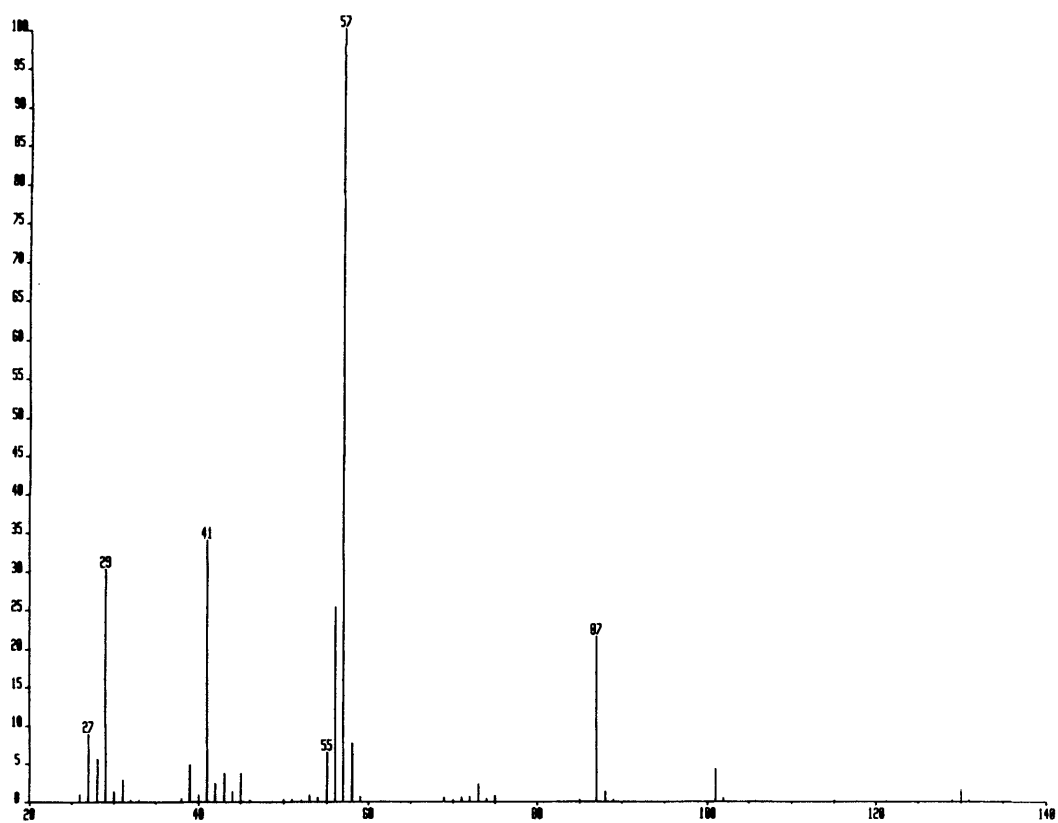


Figure 2.2

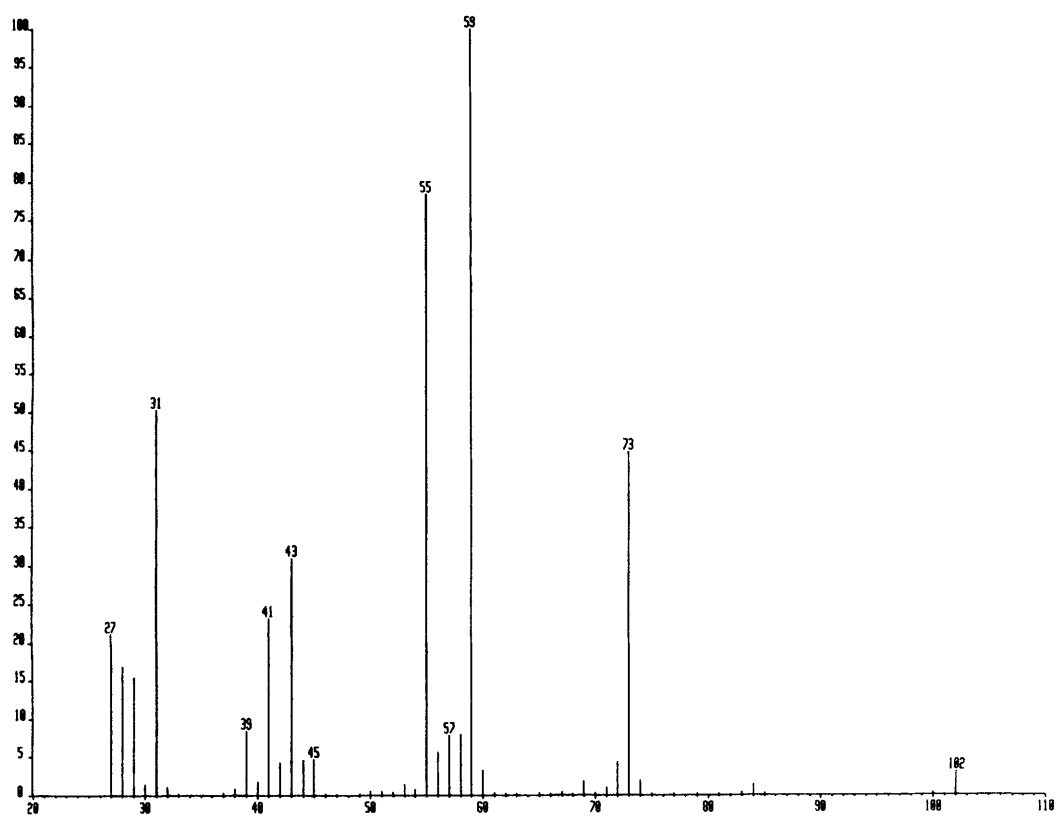
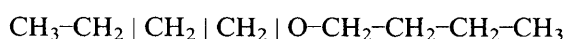


Figure 2.3

As soon as we introduce a different atom into our molecule, the simple picture we have seen for octane changes. Figure 2.2 shows the mass spectrum of di-*n*-butyl ether,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ . We have a molecular ion at 130, but only three fragmentations, one of which dominates. These are:

Molecular ion		Ion		Mass lost	Possible fragment
130	–	101	=	29	$\text{C}_2\text{H}_5$
130	–	87	=	43	$\text{C}_3\text{H}_7$
130	–	57	=	73	$\text{C}_4\text{H}_9\text{O}$

In this case, the oxygen atom affects the pattern of splitting of the molecule by stabilising the ion containing oxygen; the main splitting is that of the C–O bond. Loss of  $\text{C}_3\text{H}_7$  also occurs because the ion  $\text{CH}_2=\text{O}^+\text{C}_4\text{H}_9$  is also strongly stabilised by the oxygen (a nitrogen heteroatom gives a similar stabilisation and splitting):

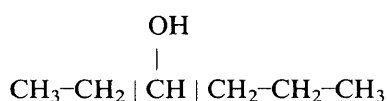


The next spectrum returns to one of the persistent problems of mass spectrometry, which is to identify the molecular ion. This is particularly difficult with the spectra of alcohols, where the molecular ion is often small or absent, as is shown in Figure 2.3, the spectrum of hexan-3-ol,  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$ .

The small peak at  $m/z$  102 is the molecular ion. The main fragmentations of the ion are:

Molecular ion		Ion		Mass lost	Possible fragment
102	–	73	=	29	$\text{C}_2\text{H}_5$
102	–	59	=	43	$\text{C}_3\text{H}_7$
102	–	55	=	47	
102	–	43	=	59	$\text{C}_3\text{H}_9\text{O}$

The main splittings are thus:



The –OH group stabilises an ion generated at the carbon to which it is attached, so splitting of either of the C–C bonds to that carbon atom is favoured.

Note that we have not considered the peak at  $m/z$  55, which has resulted from splitting off a mass of 47. There is not a reasonable fragment of mass 47 which can split off hexan-3-ol. The peak at  $m/z$  55 probably arises after an initial dehydration of hexan-3-ol to hexene. Loss of water (mass 18 Daltons) would give hexene, molecular weight 84. The spectrum in fact shows a small peak at  $m/z$  84. If hexene loses  $\text{C}_2\text{H}_5$  (mass 29 Daltons), then we would expect a peak at  $m/z$  55.

If we had made an error in our choice of the molecular ion peak, then the observed fragmentations would have been impossible. Suppose we thought the molecular ion was at  $m/z$  84, which is possible since it involves an even mass. The peak at  $m/z$  73 would then involve loss of 11 Daltons, and that at 59

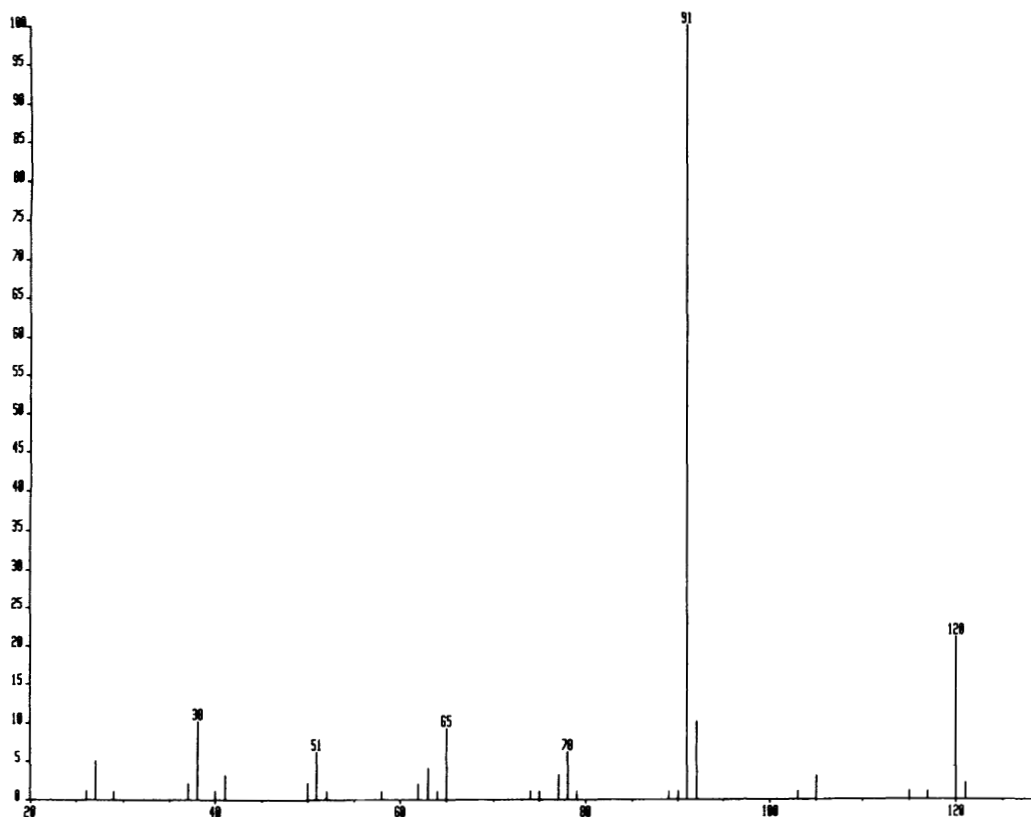


Figure 2.4

the loss of 25 Daltons. Neither fragmentation involves a reasonable ion, so, clearly, something is wrong.

If we have the mass spectrum of a molecule containing an aromatic ring, then we should expect to find a peak from a very stable ion, the benzyl ion,  $\text{PhCH}_2^+$ , provided the structure permitted this ion to form. An unsubstituted benzyl peak is found at  $m/z$  91; substitution will obviously change the mass of the ion. Formation of a benzyl ion is shown in the next spectrum, Figure 2.4, which shows the mass spectrum of propylbenzene,  $\text{PhCH}_2\text{CH}_2\text{CH}_3$ .

The spectrum shows a large molecular ion peak at  $m/z$  120, and a single large peak at  $m/z$  91, resulting from the loss of 29 Daltons, consistent with the loss of  $\text{C}_2\text{H}_5$ . The peak at  $m/z$  91 is the benzyl ion, and the molecule shows a single fragmentation:



If an aromatic molecule cannot form a benzyl ion, then the phenyl ion  $\text{C}_6\text{H}_5^+$ ,  $m/z$  77, may be formed, but formation of the benzyl ion is favoured.

The next spectrum is that of octan-3-one,  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , shown in Figure 2.5.

On the basis of our analysis of the spectrum of hexan-3-ol, we would expect this molecule to split on each side of the carbonyl carbon atom, since this would yield a stabilised acylium ion,  $\text{R--C=O}^+$ . The spectrum shows that this is in fact observed:

Molecular ion		Ion		Mass lost	Possible fragment
128	–	99	=	29	$\text{C}_2\text{H}_5$
128	–	72	=	56	
128	–	57	=	71	$\text{C}_5\text{H}_{11}$

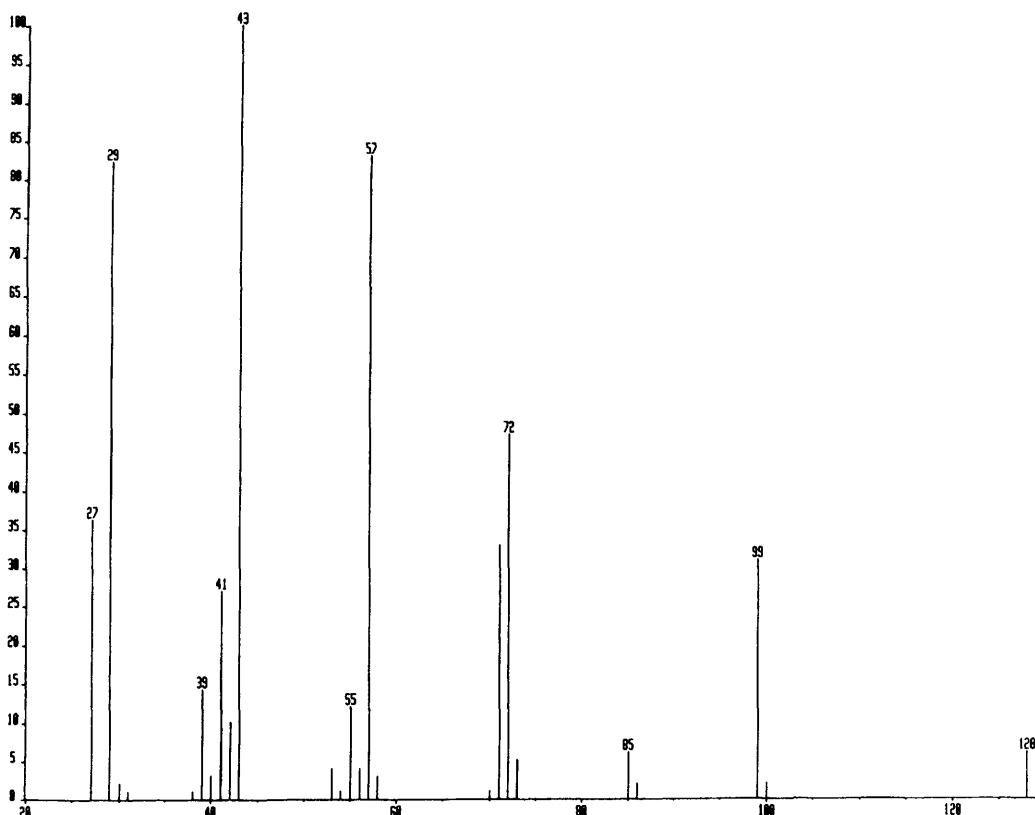


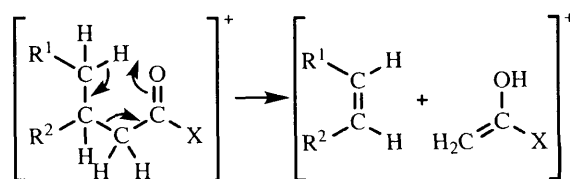
Figure 2.5

These splittings yield peaks at  $m/z$  99 and 57. There is, however, another peak at  $m/z$  72. It has an *even*  $m/z$  value; all major peaks which we have observed previously have odd  $m/z$  values. It is a general guideline that the mass spectrum of an organic compound containing no element other than carbon, hydrogen, oxygen and the halogens has an even  $m/z$  molecular ion and odd  $m/z$  fragment ions.

So far, we have noted two variations on this rule:

- A. The molecule contains an odd number of nitrogen atoms. In this case, the molecular ion will have an odd  $m/z$  ratio, and fragment ions containing an odd number of nitrogen atoms an even  $m/z$  ratio.
- B. The molecule has undergone an elimination reaction to give a stable product. We have already seen that hexan-3-ol, which has a molecular ion at  $m/z$  102, can lose water to give hexene, which has a molecular ion at  $m/z$  84. Carboxylic acids often lose  $\text{CO}_2$  (mass 44 Daltons) to give an ion of even  $m/z$  ratio; loss of  $\text{HCl}$  (masses 36 and 38 Daltons) and  $\text{HBr}$  (masses 80 and 82 Daltons) and loss of ethene (mass 28 Daltons) are also observed. Such peaks are often small.

This observation now adds a third reason for a peak to have an even  $m/z$  ratio, namely the McLafferty rearrangement:



The McLafferty rearrangement occurs whenever we have a carbonyl compound which has a  $\gamma$ -hydrogen atom in a position which permits it to migrate to the carbonyl oxygen atom through a cyclic transition state. The reaction can occur with any type of carbonyl group, and the  $m/z$  ratio of the even peak tells us what other substituents there are on the carbonyl carbon atom (Table 2.3). If we have an amide, so that  $X = \text{NH}_2$ , then the McLafferty rearrangement gives a peak of odd  $m/z$  ratio, 59. If the carbonyl group has a substituent on the neighbouring carbon atom, then a McLafferty rearrangement gives a different size of even  $m/z$  peak.

**Table 2.3** Ions characteristic of McLafferty rearrangements

Compound	$X$	Ion ( $m/z$ )
Aldehyde	H	44
Methyl ketone	$\text{CH}_3$	58
Carboxylic acid	OH	60
Ethyl ketone	$\text{CH}_3$	72
Methyl ester	$\text{OCH}_3$	74
Ethyl ester	$\text{OC}_2\text{H}_5$	88

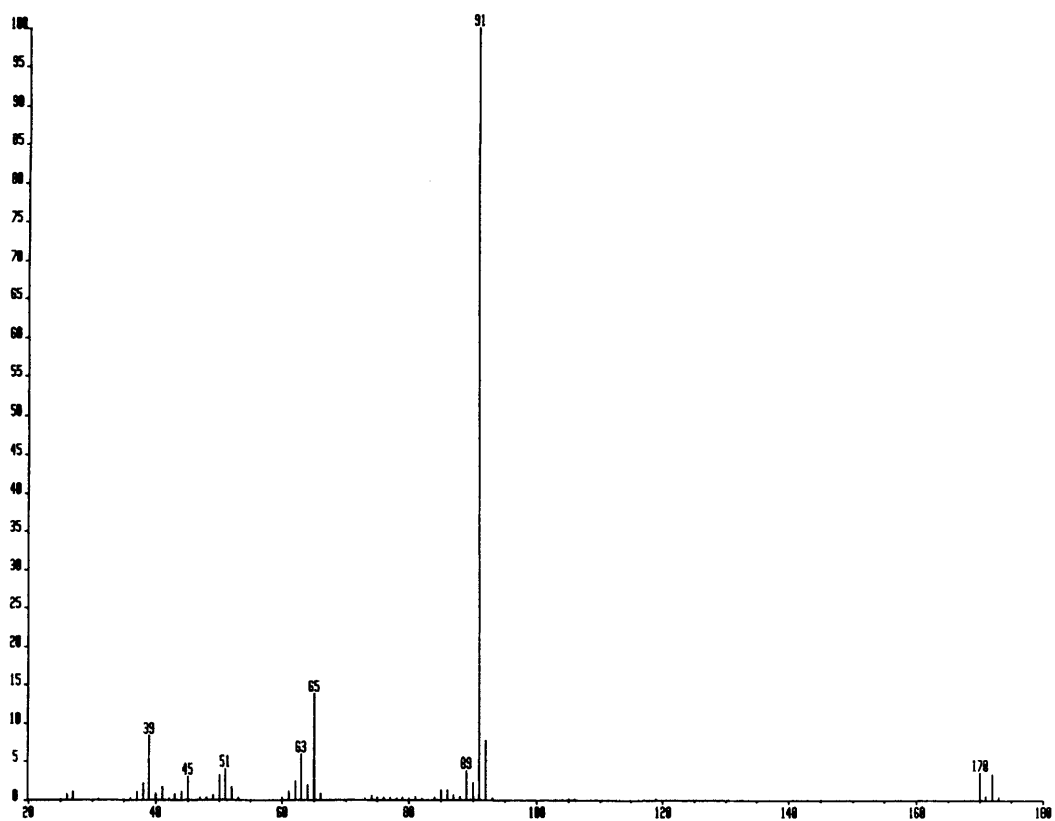
## Summary

When we first look at a mass spectrum, we should look for:

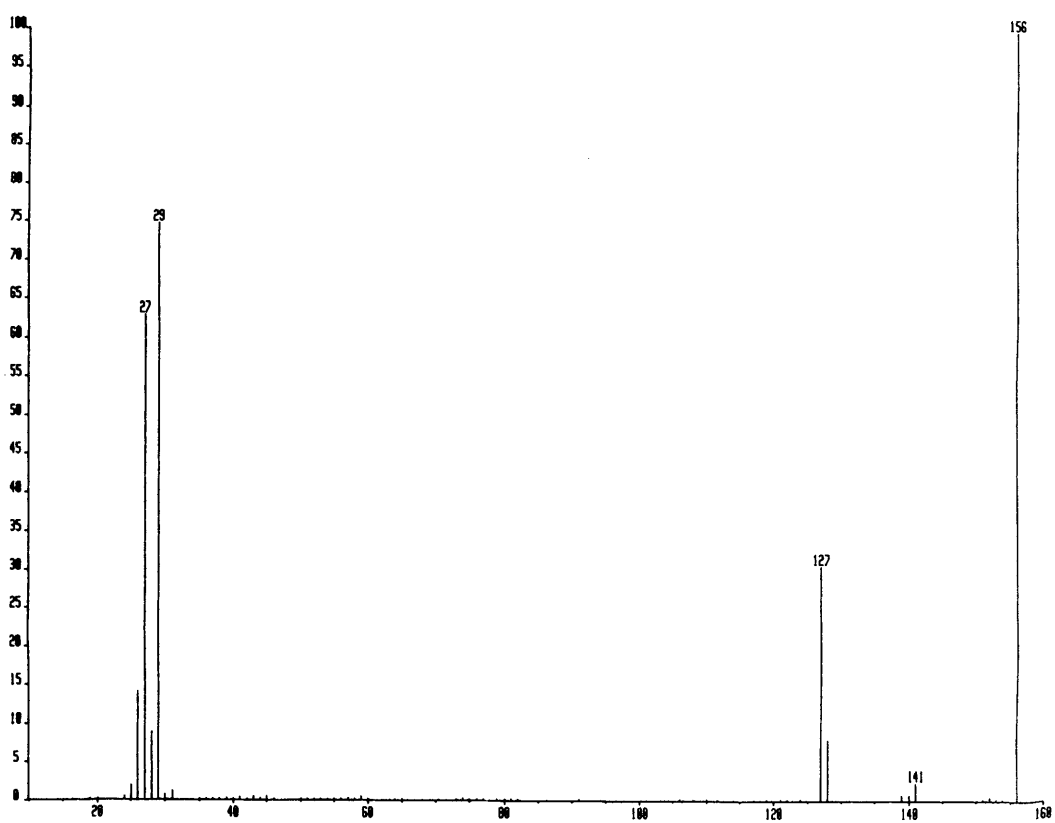
- The molecular ion. This often, but not always, has an even  $m/z$  ratio, and it may be very small.
- The presence of the halogens. Bromine and chlorine are readily spotted by peak patterns; bromine has two equal peaks two mass units apart, while chlorine has two peaks in the ratio 3 to 1 which are also two mass units apart. Iodine can be spotted from sheer size: it has an atomic weight of 127.
- Any major ion of even  $m/z$  ratio. If the molecular ion has an odd  $m/z$  ratio, then the ion contains an odd number of nitrogen atoms; if it has an even  $m/z$  number, then you probably have an elimination reaction or a McLafferty rearrangement of a carbonyl compound. Look also for ions at  $m/z$  91 (possibly benzyl) and  $m/z$  77 (possibly phenyl).
- The main ions in the spectrum, and calculate what size of unit has been split from the molecular ion. Look at Table 2.2 to see the possible identity of the fragment split off. From this information you may be able to determine the original structure of the sample.

## Problems in Interpreting Mass Spectra

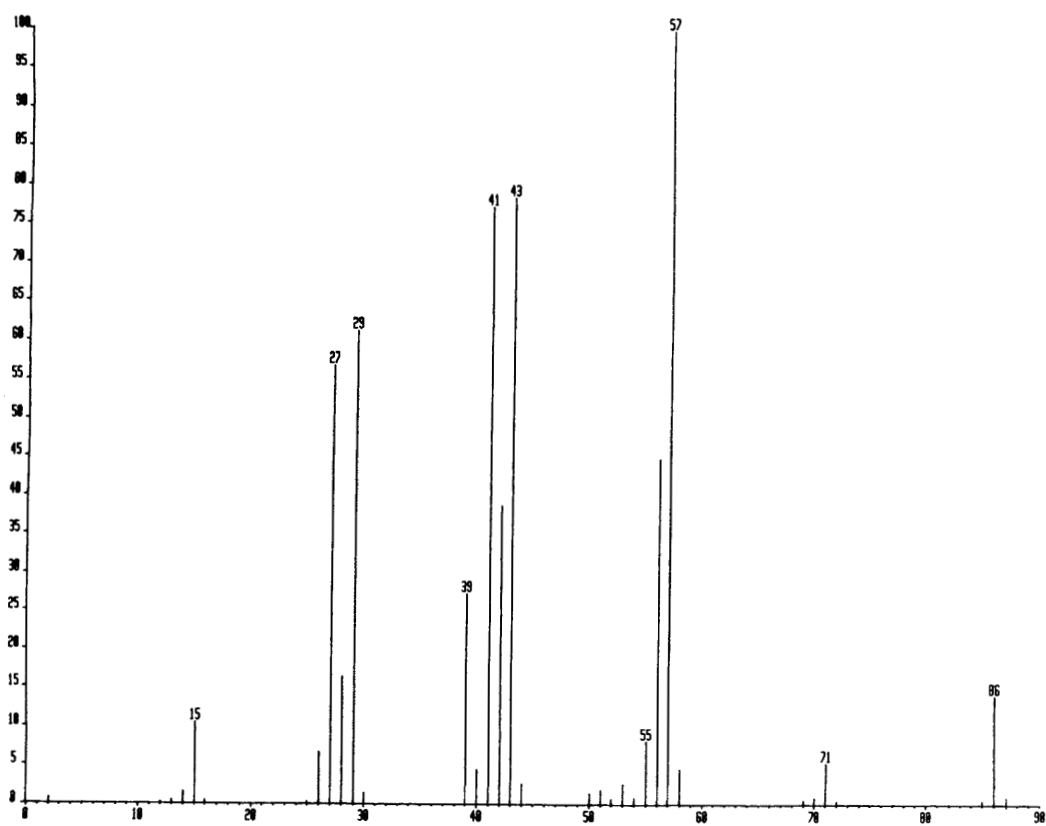
You are given the mass spectra of 20 samples. Try to identify the structures of the samples from the mass spectra.



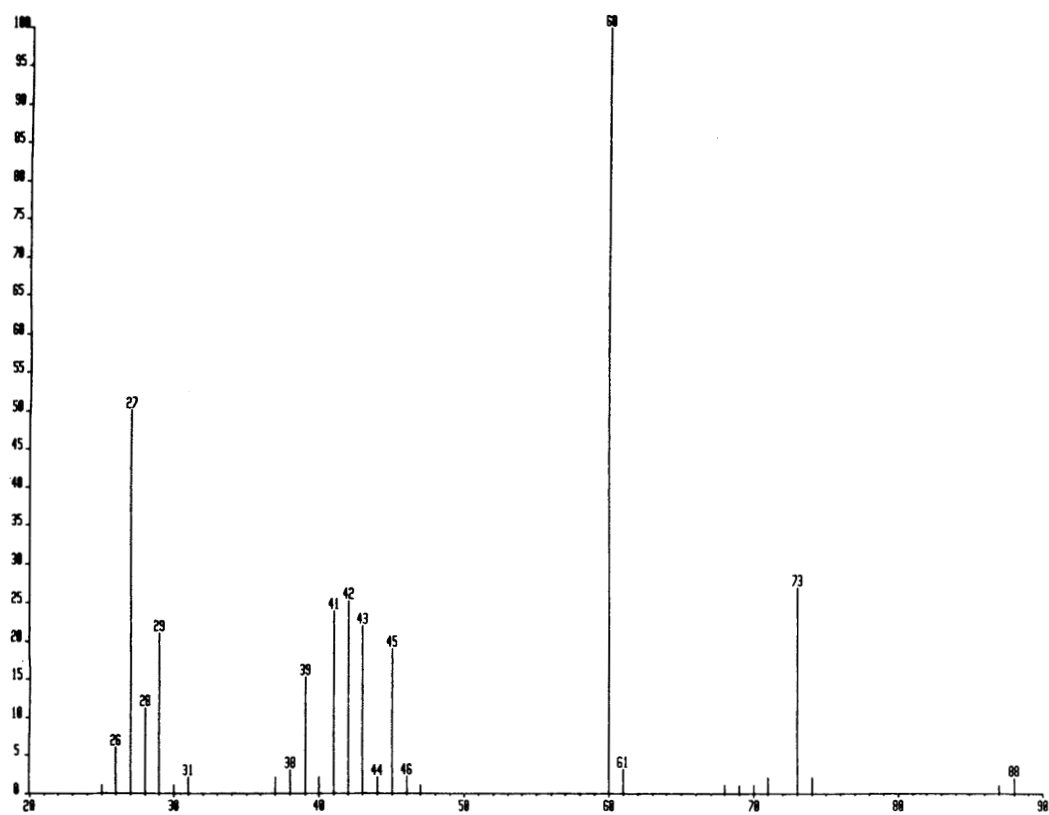
Sample 2.1



Sample 2.2

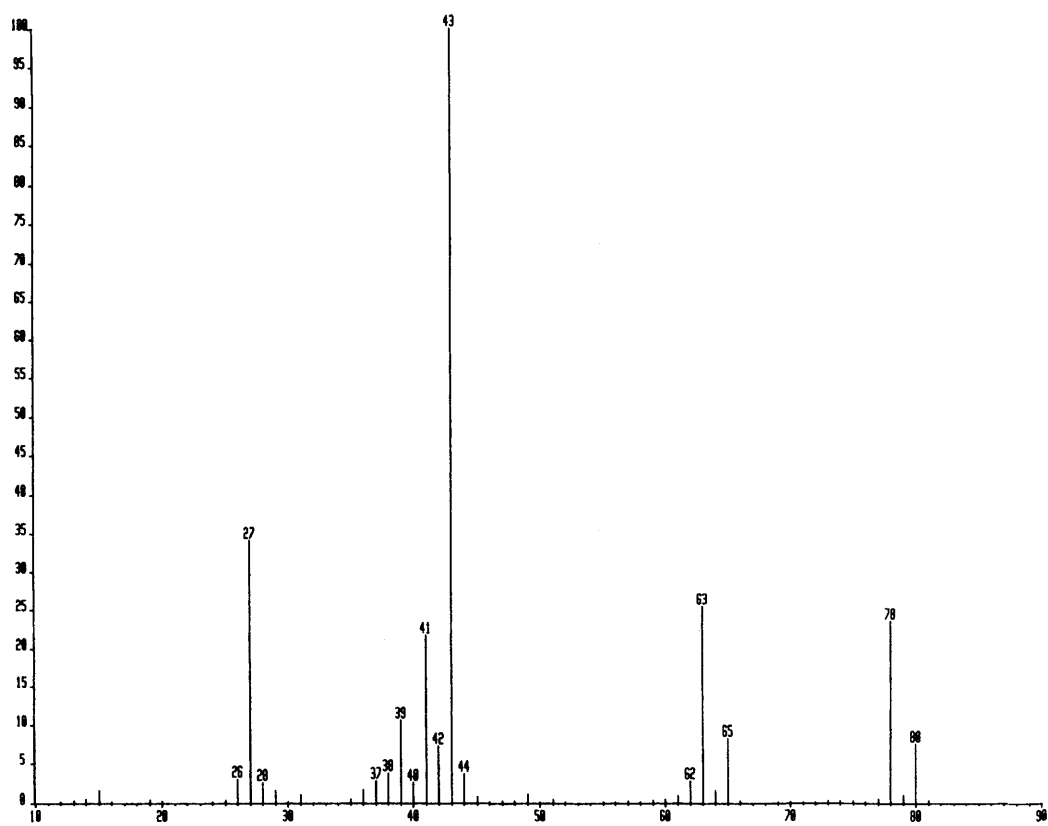


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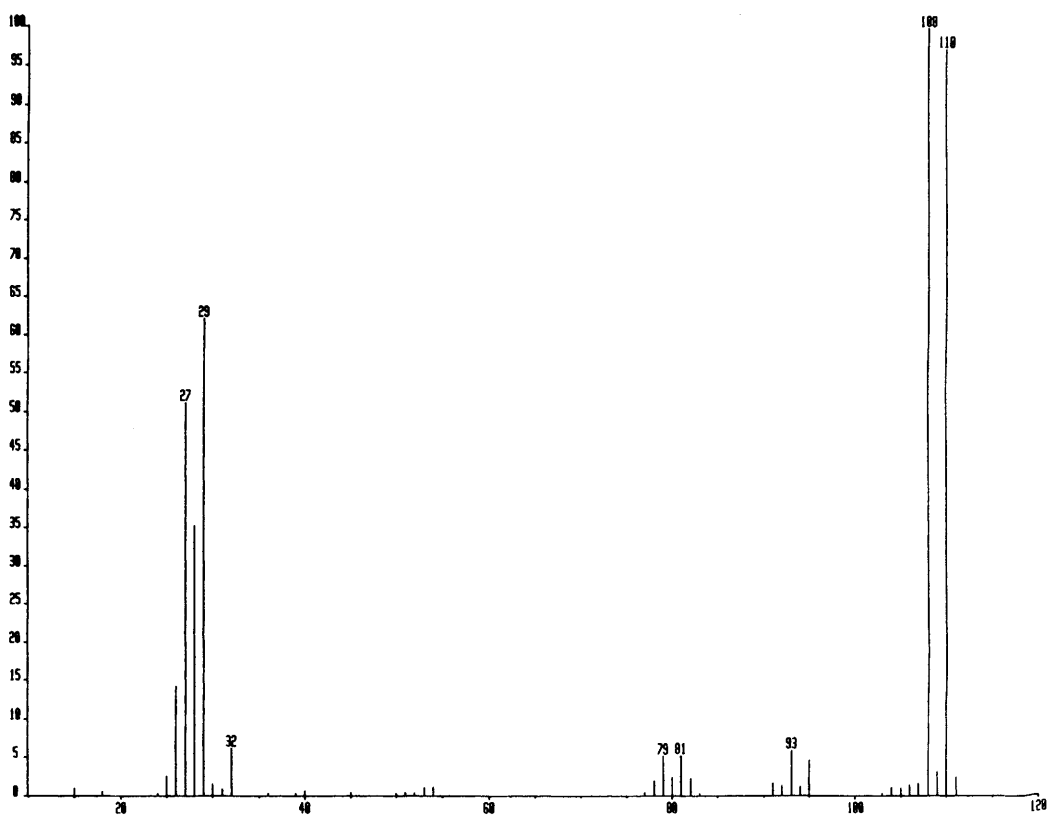


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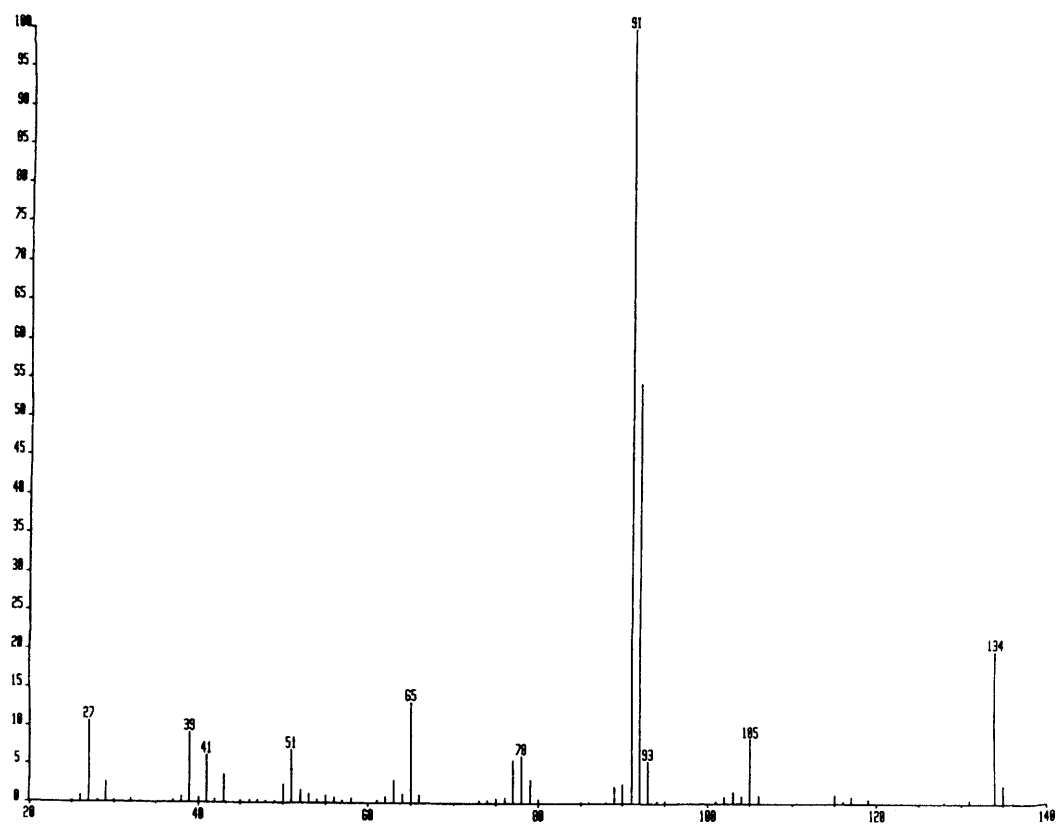




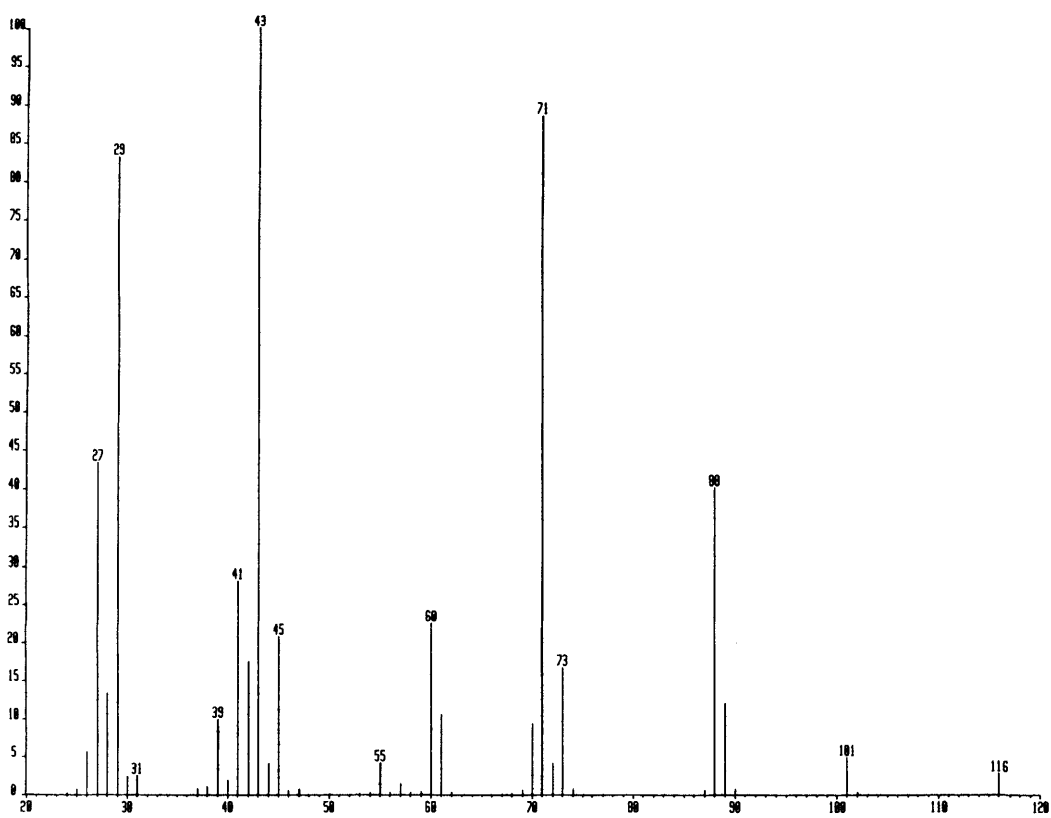
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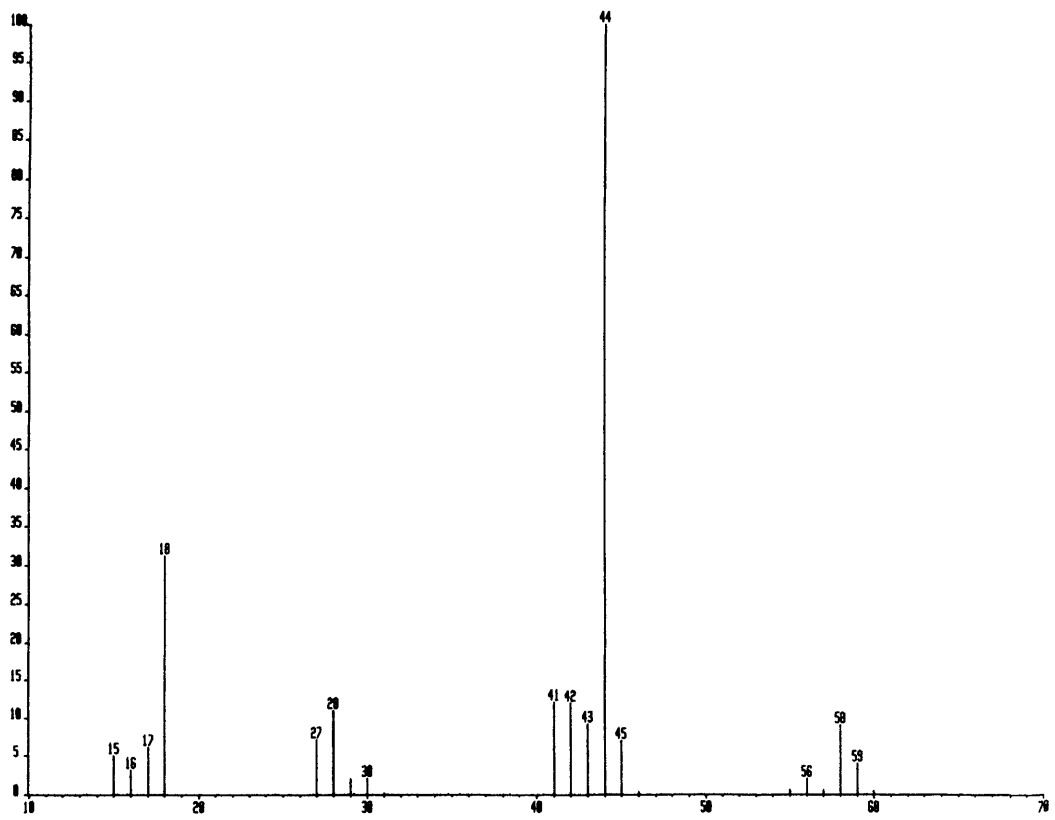
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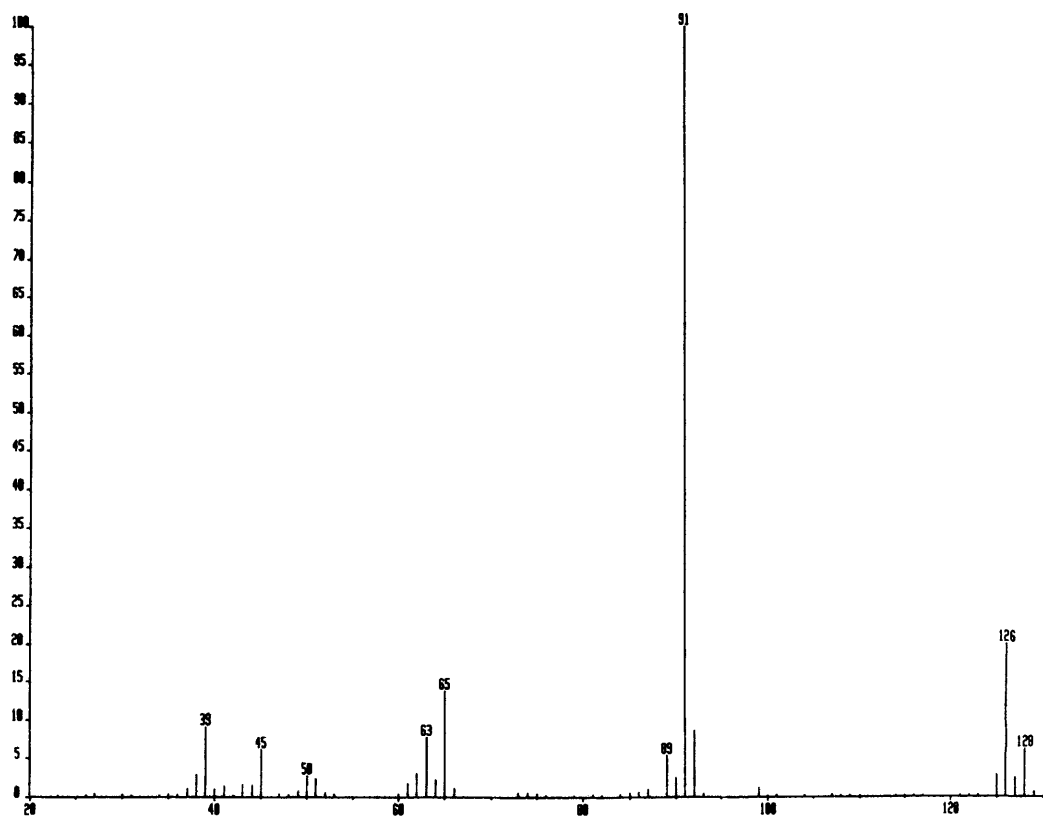
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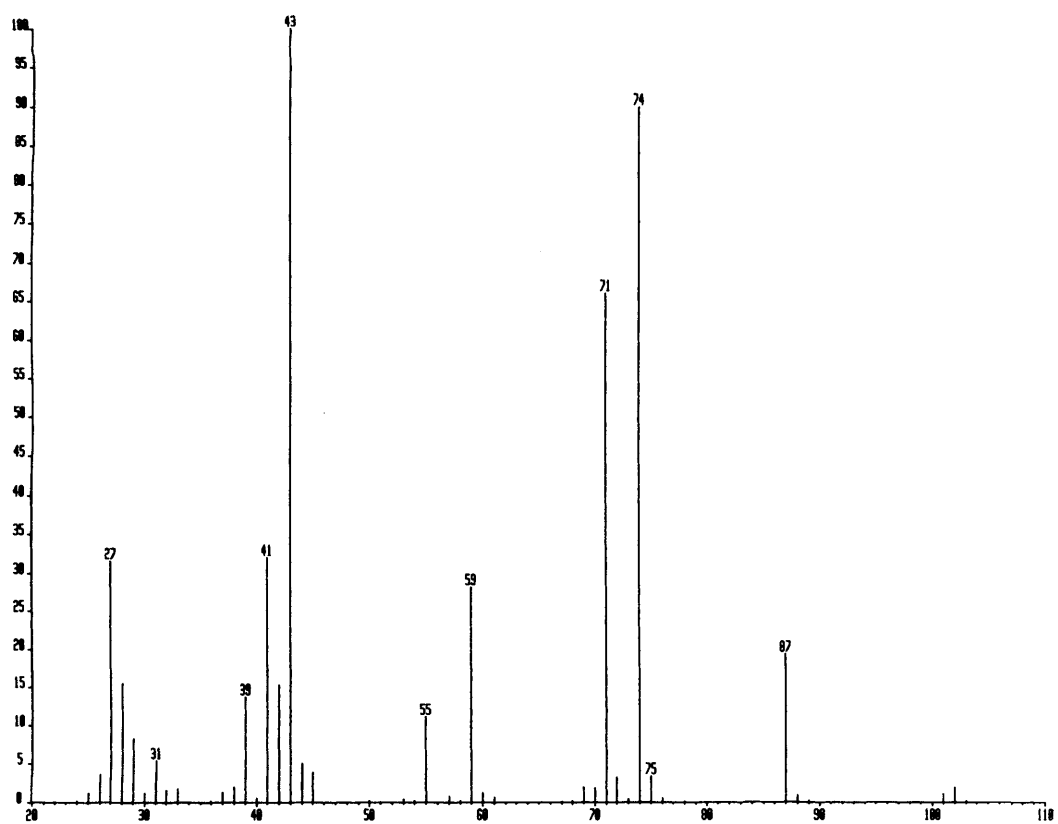
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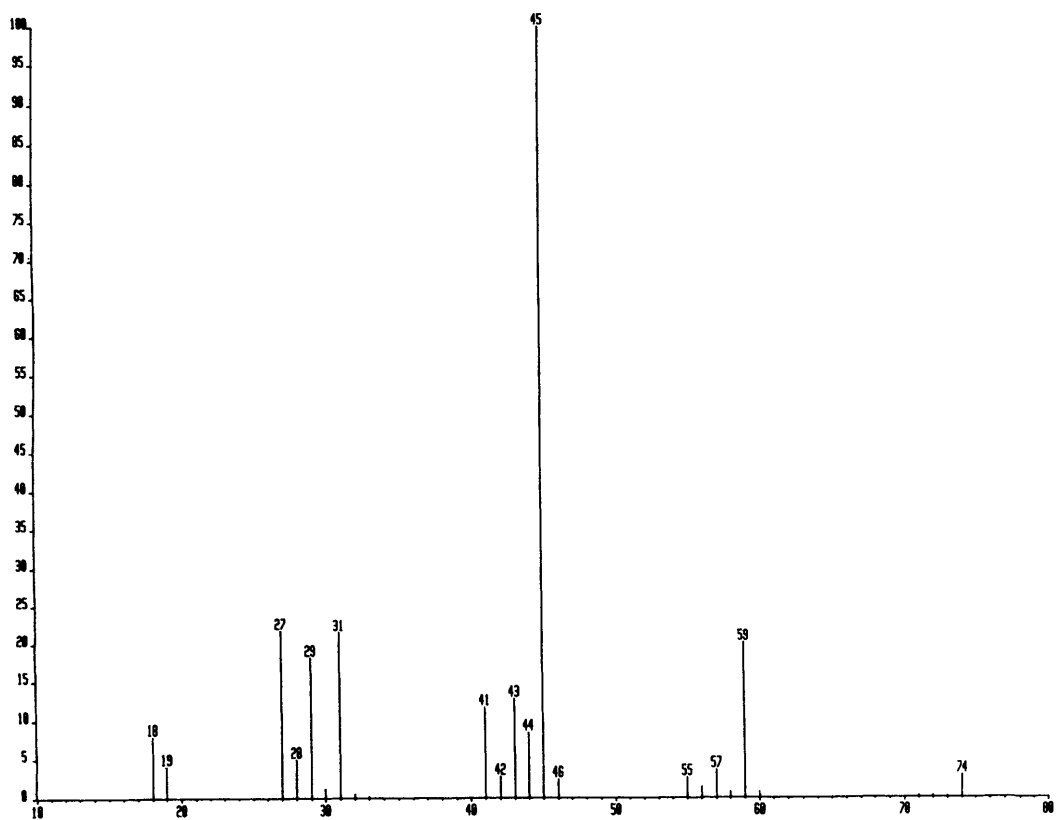
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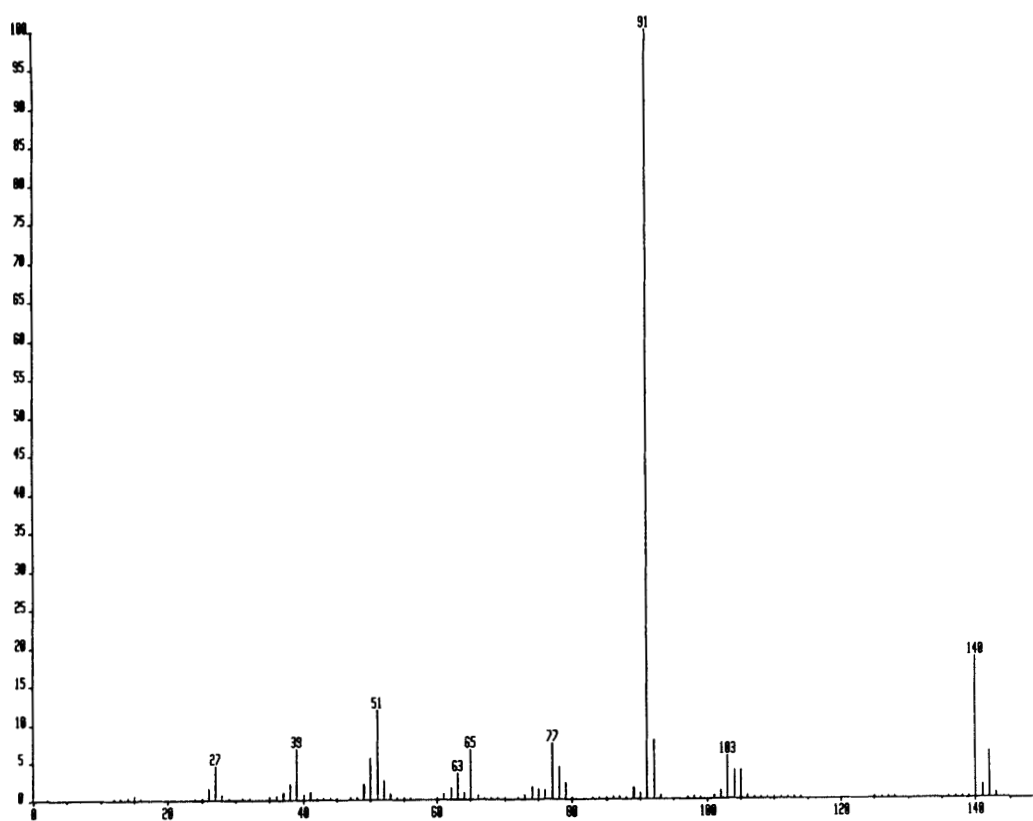
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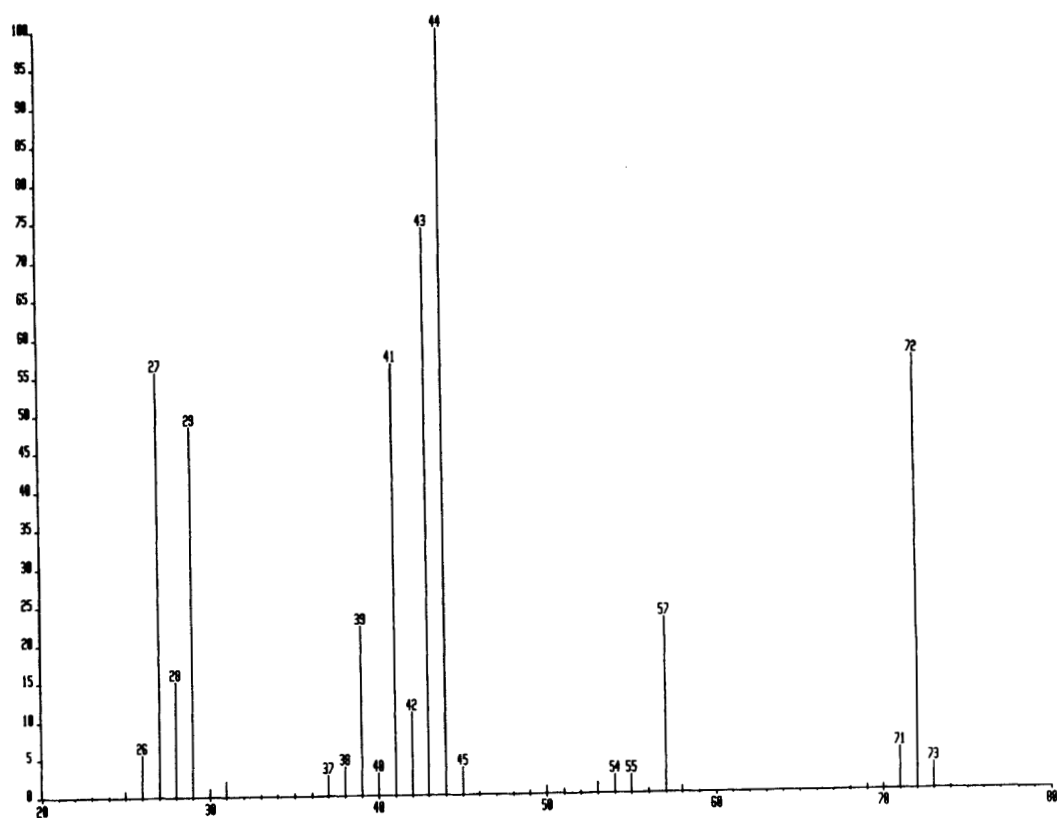
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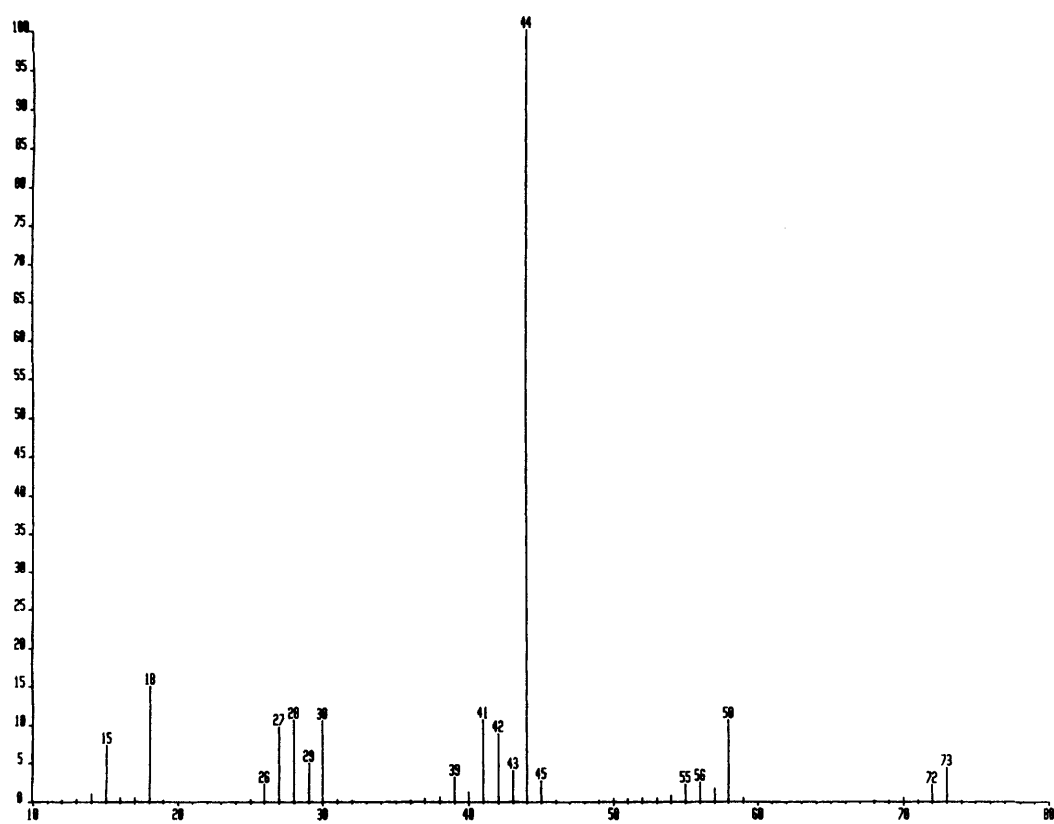
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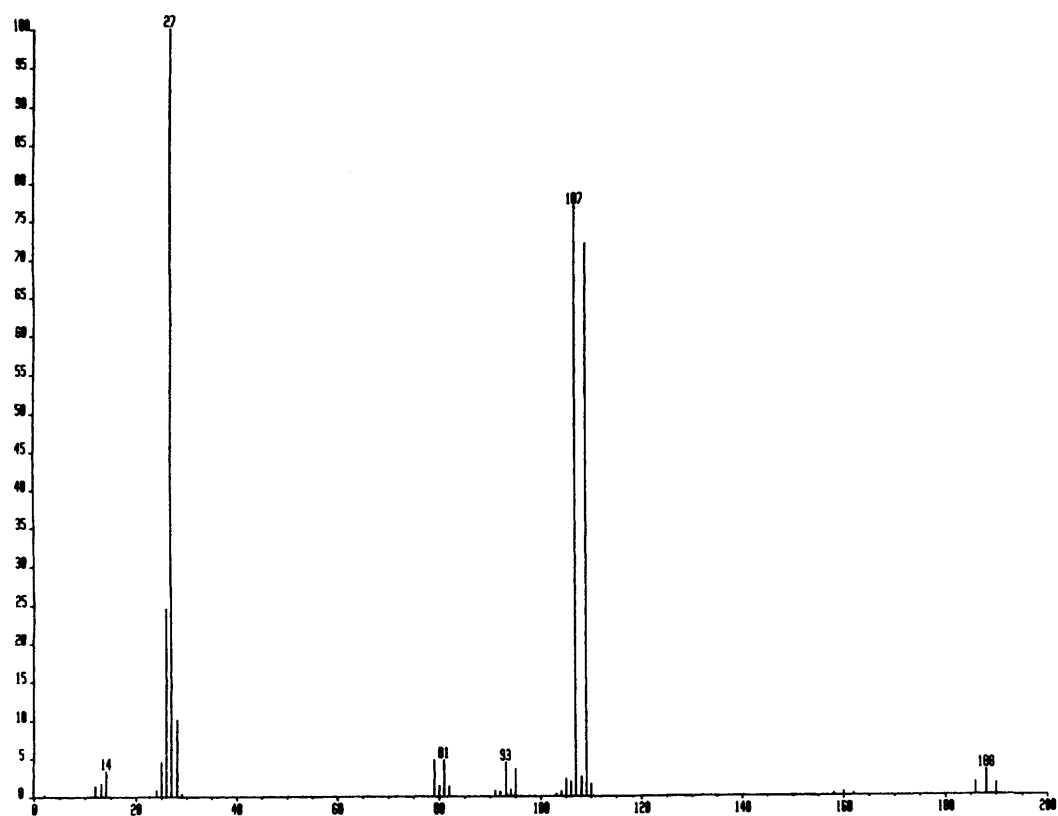
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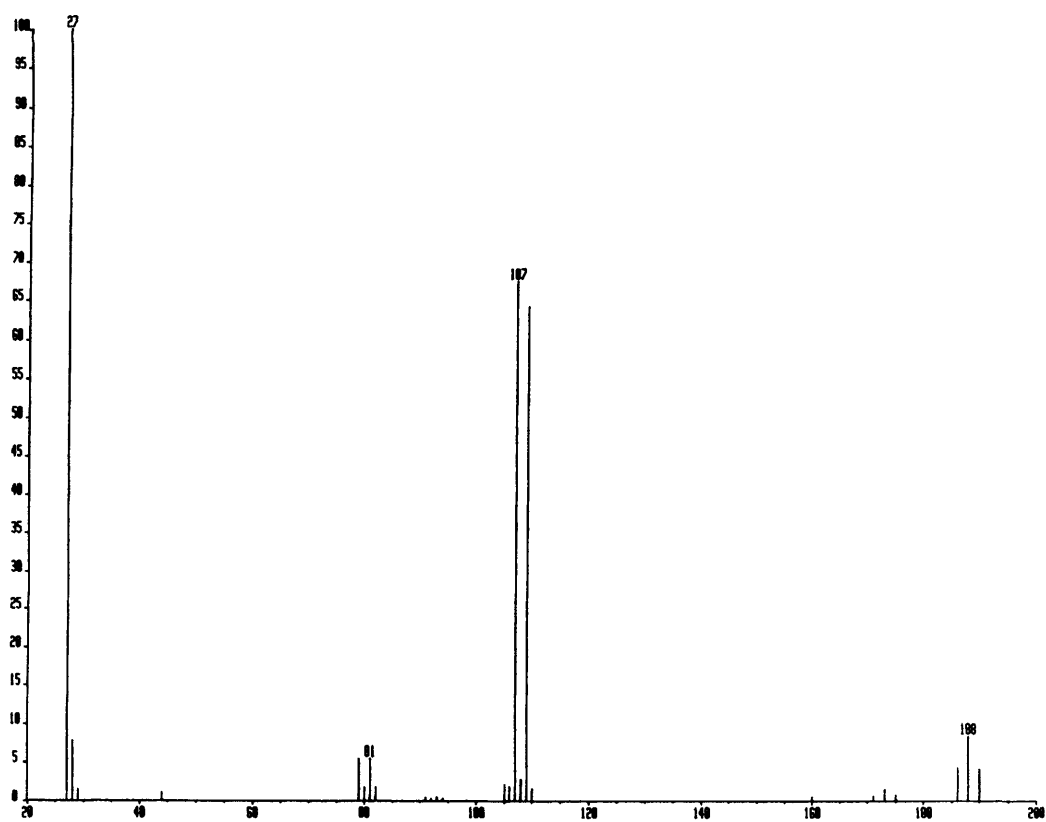
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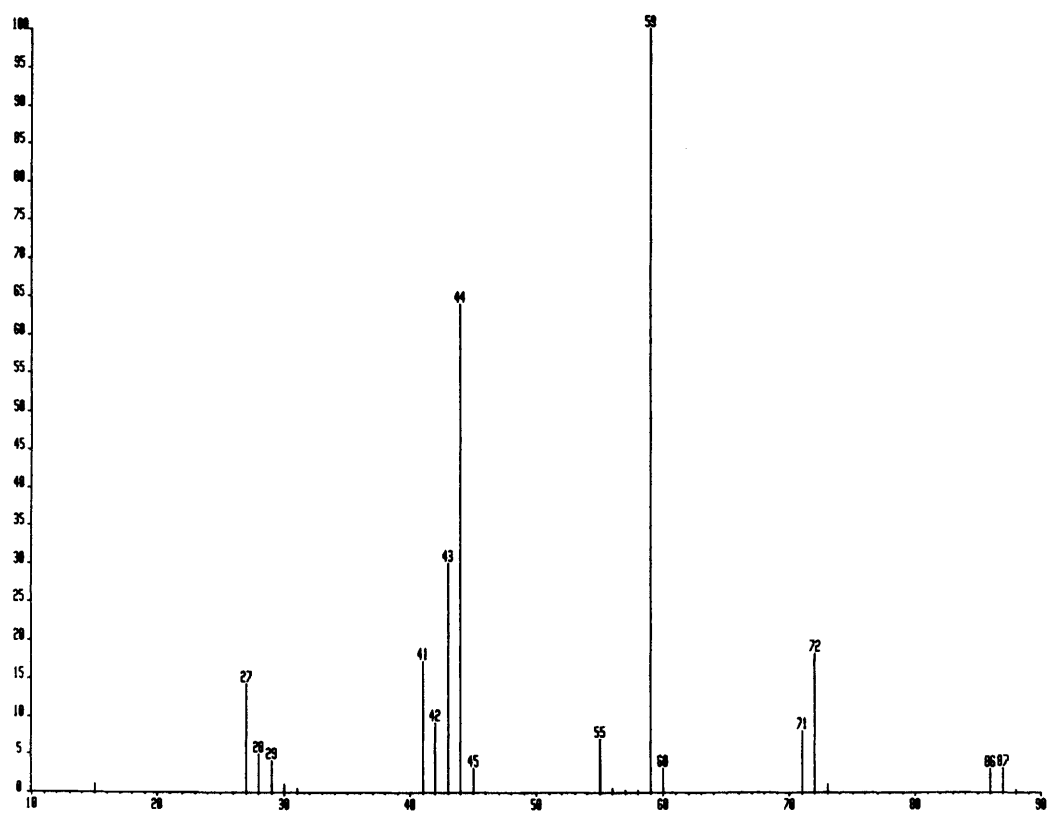
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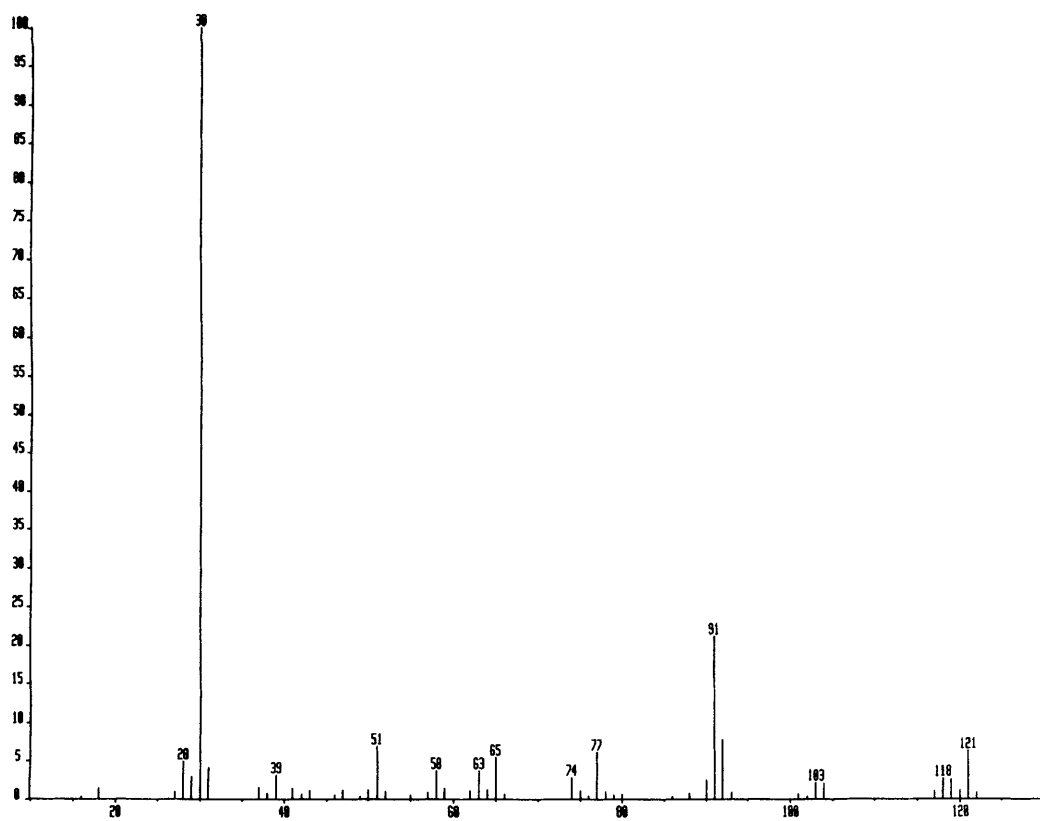
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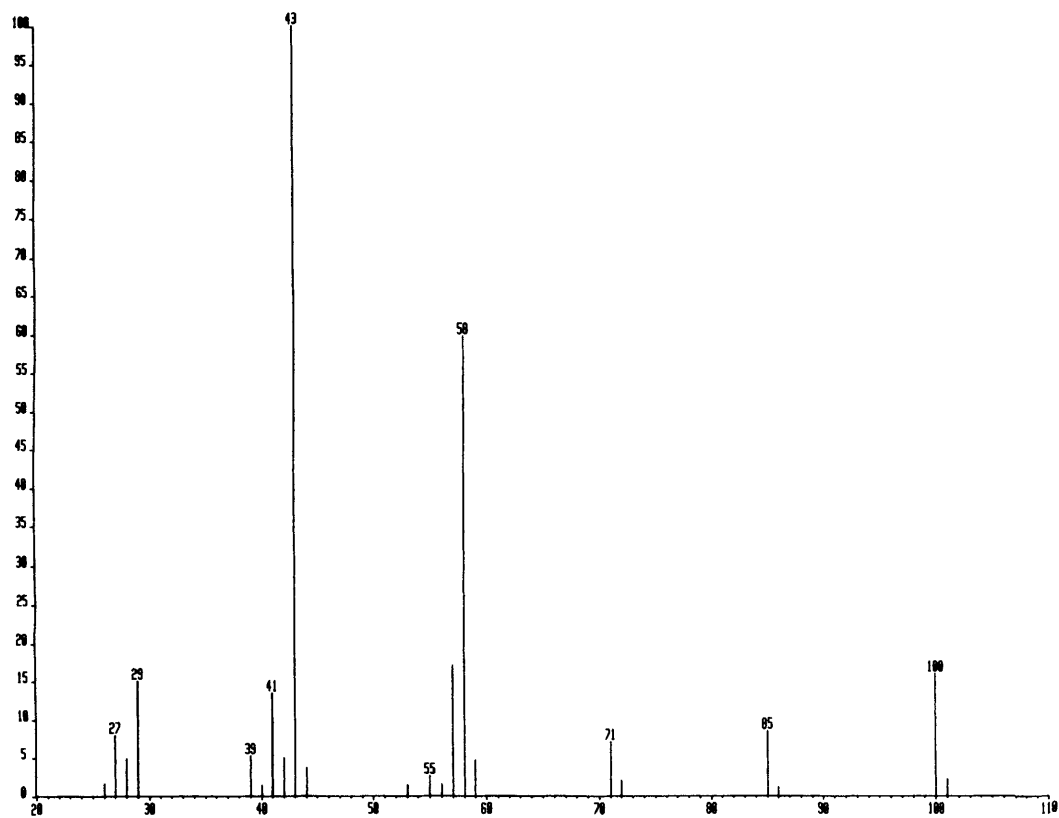
Sample 2.17



Sample 2.18



Sample 2.19

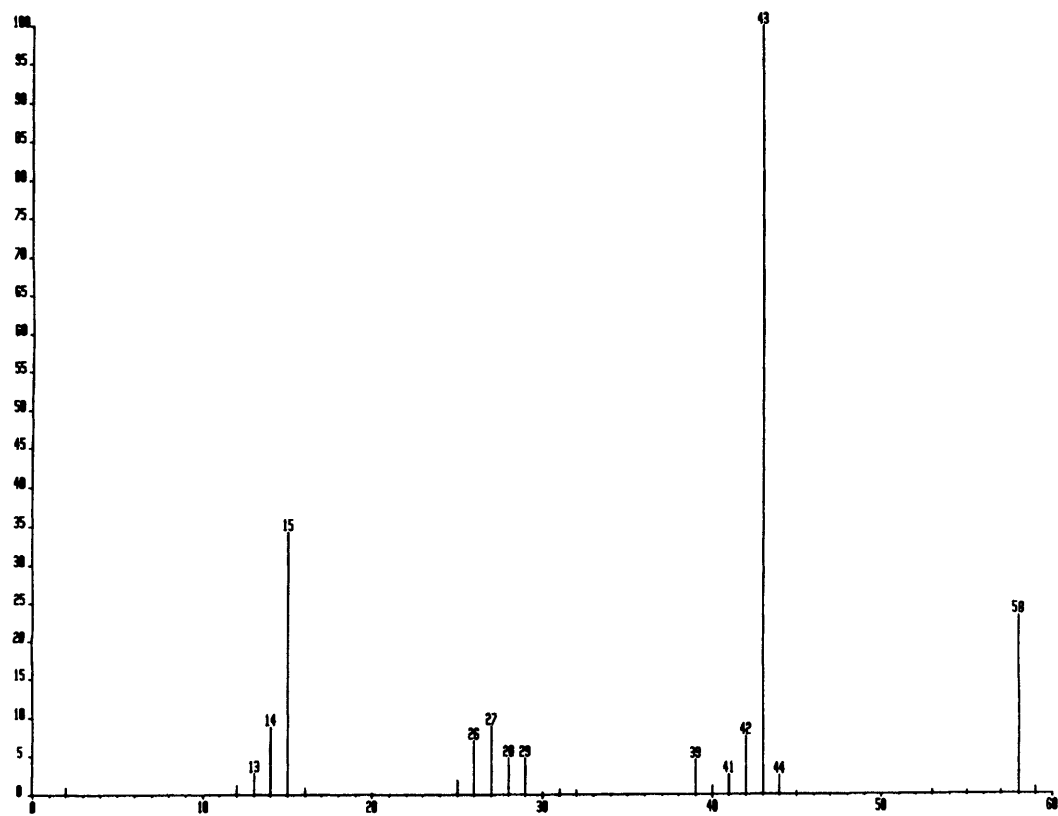
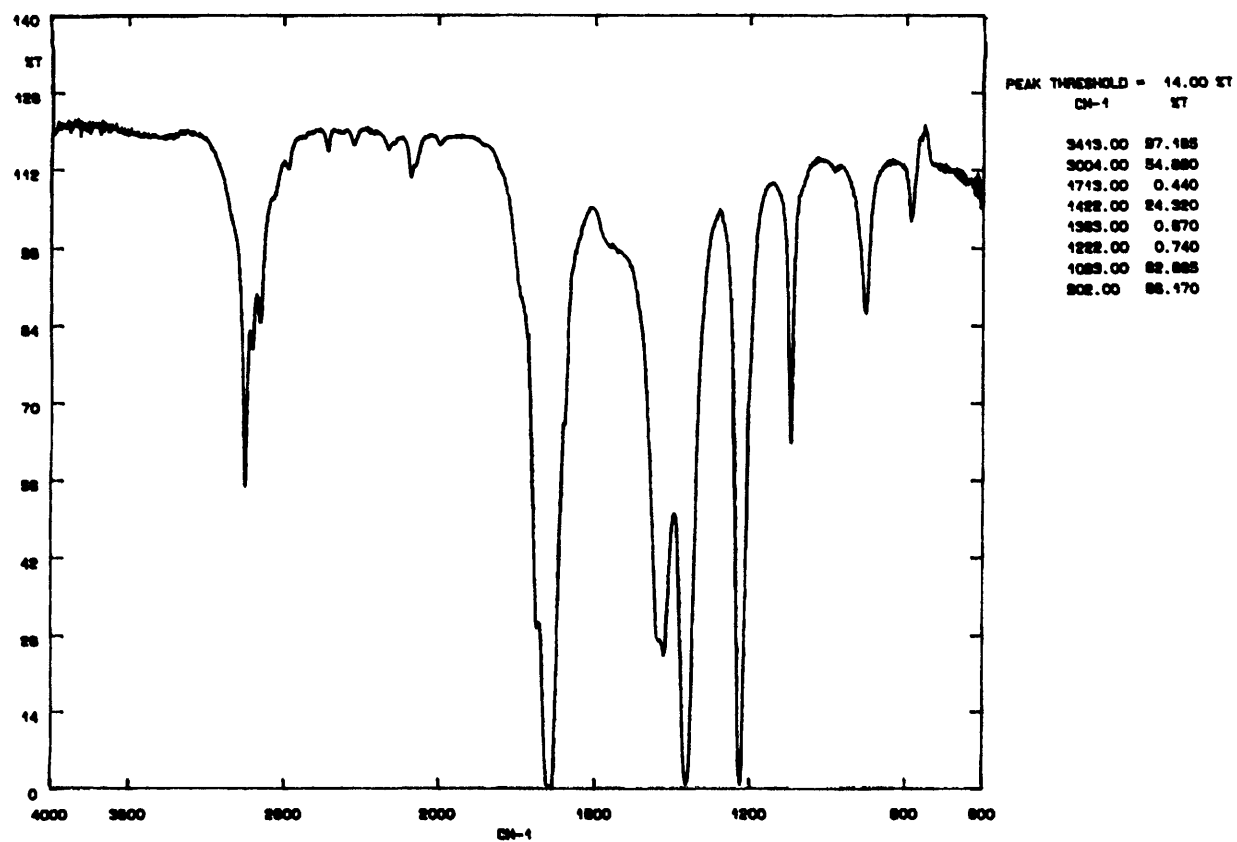


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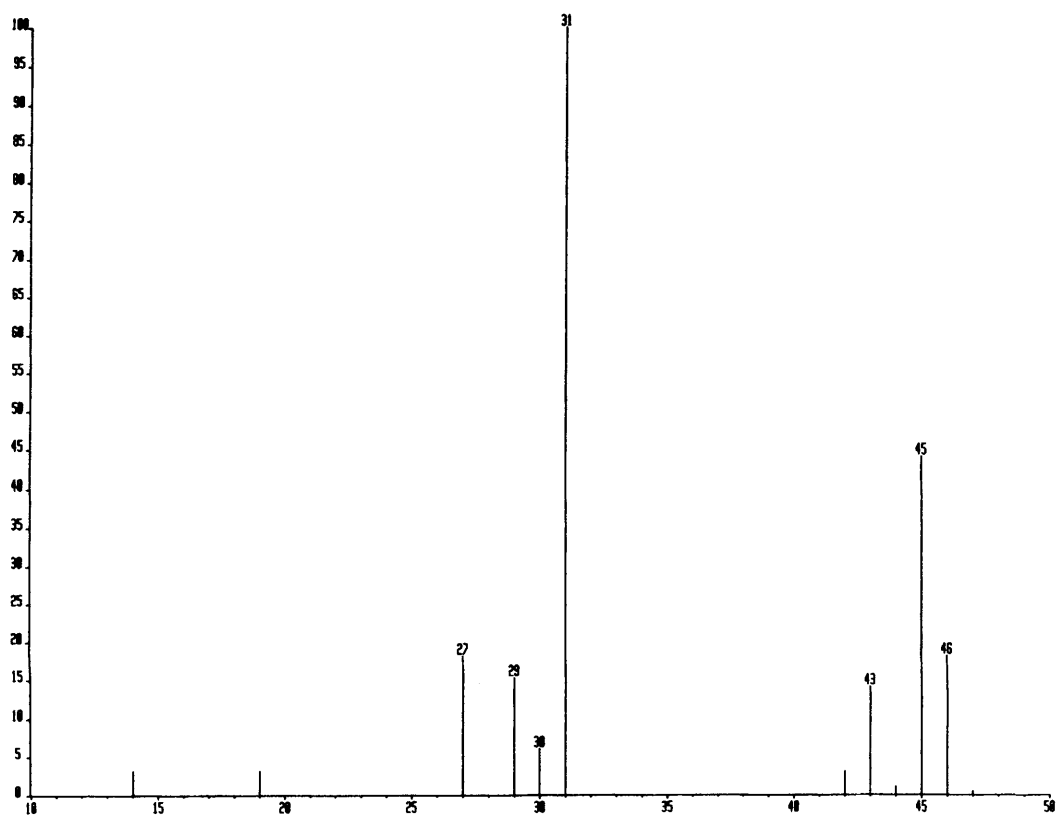
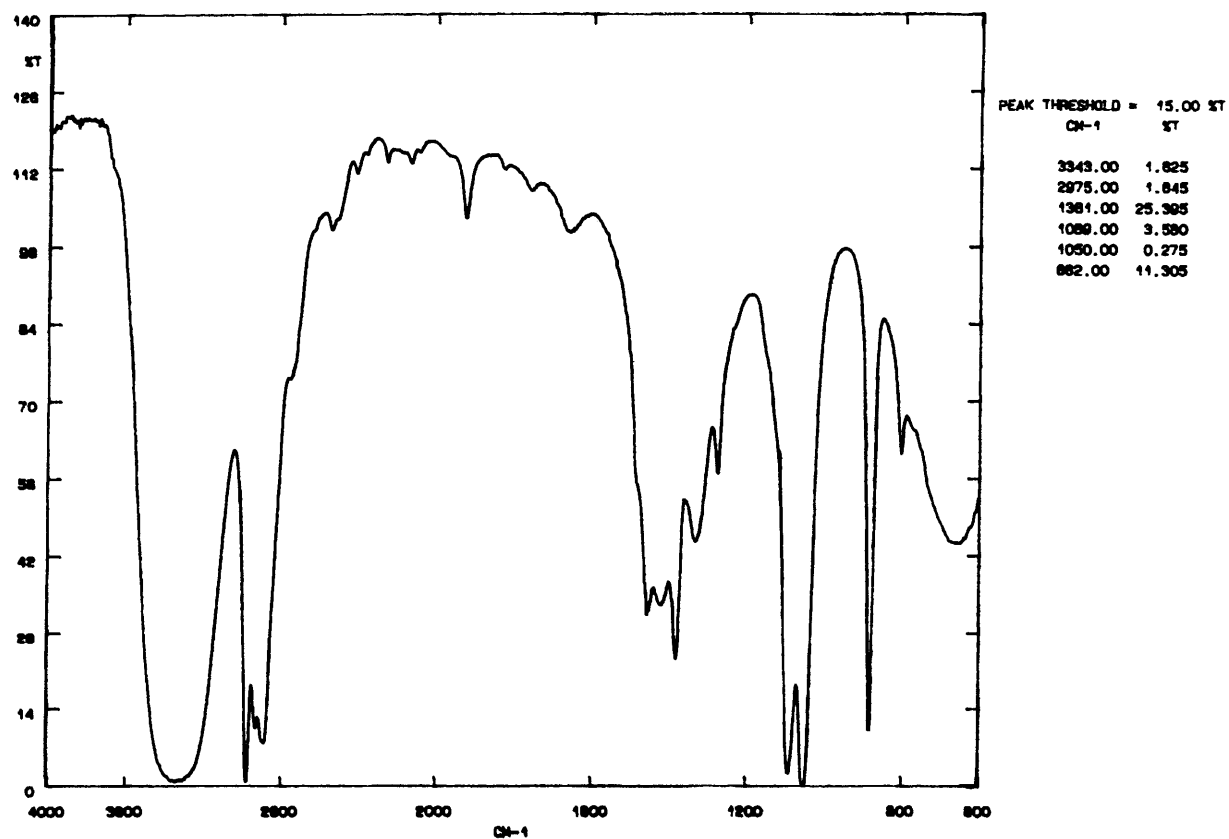


## **Problems in Interpreting Infrared Spectra and Mass Spectra**

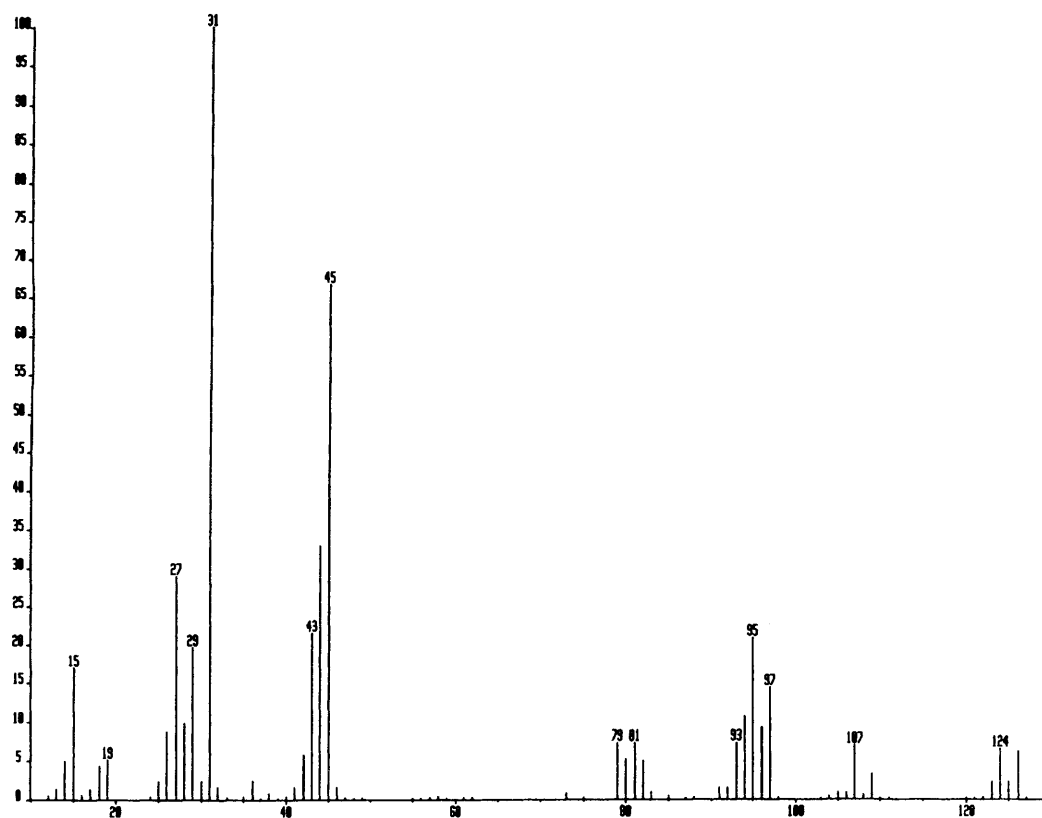
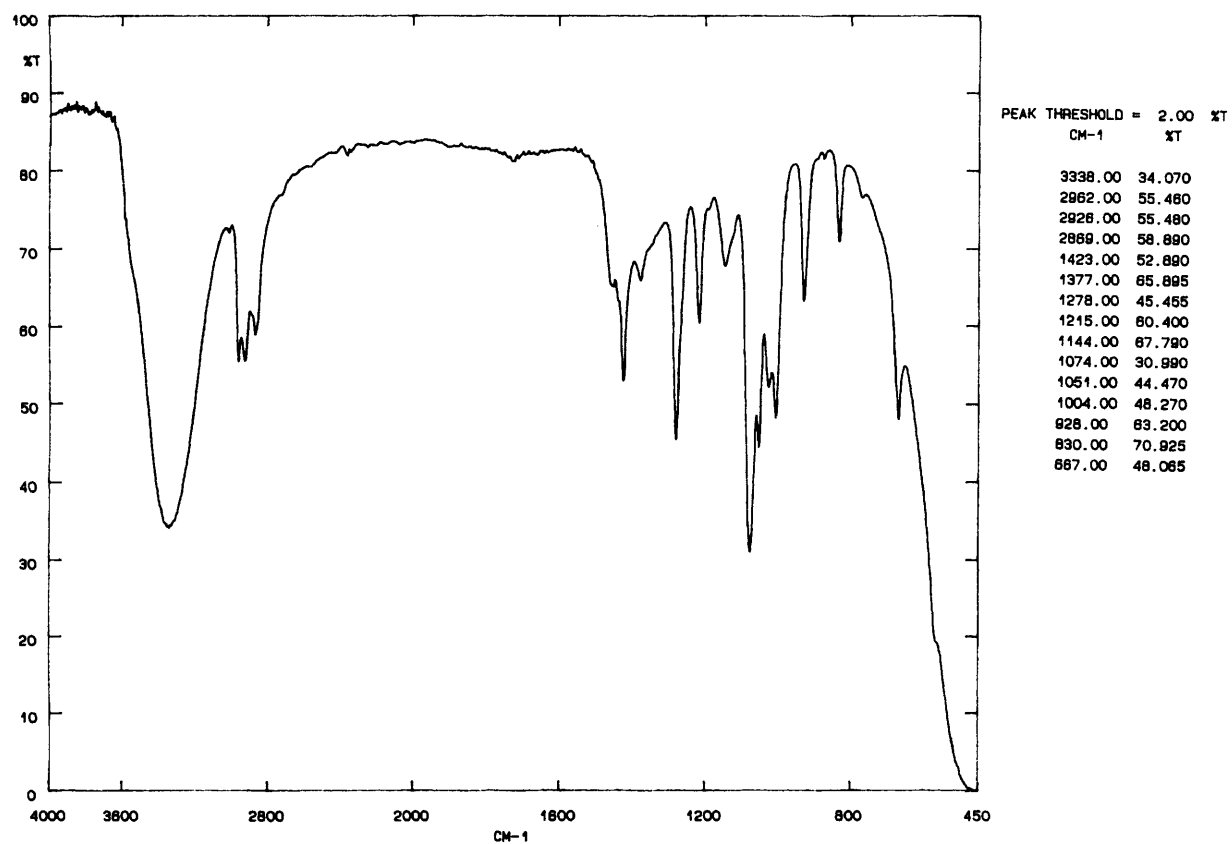
We have now seen how to identify functional groups by infrared spectroscopy and to find the molecular weight, halogen content and structural features of a molecule by mass spectrometry. If we use both techniques on a sample, then we can substantially extend the range of molecules we can identify. Both infrared spectroscopy and mass spectrometry can identify almost any molecule by comparison with a spectrum of the authentic material, but when working entirely with unknowns it is often difficult to distinguish isomers. The substances whose spectra you are given are generally simple ones, where isomerism is not a problem, so you should be able to identify each sample from its spectra.



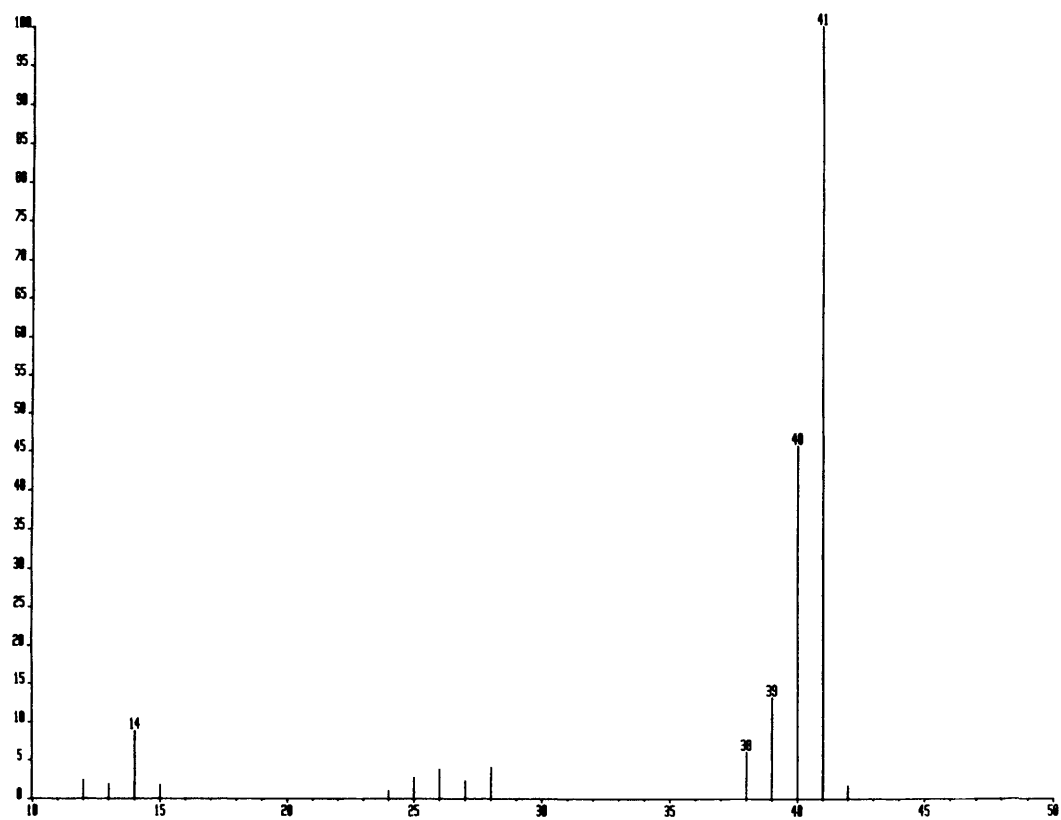
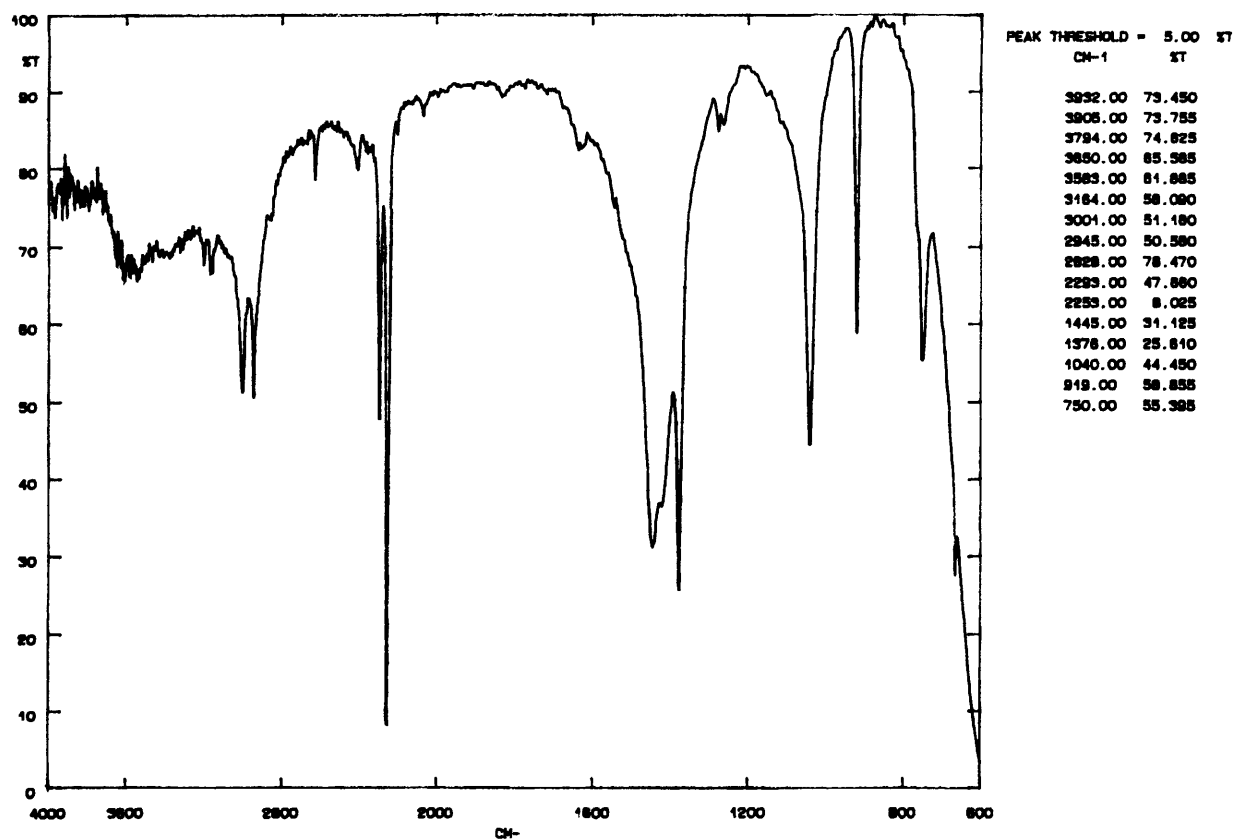
Sample 3.1



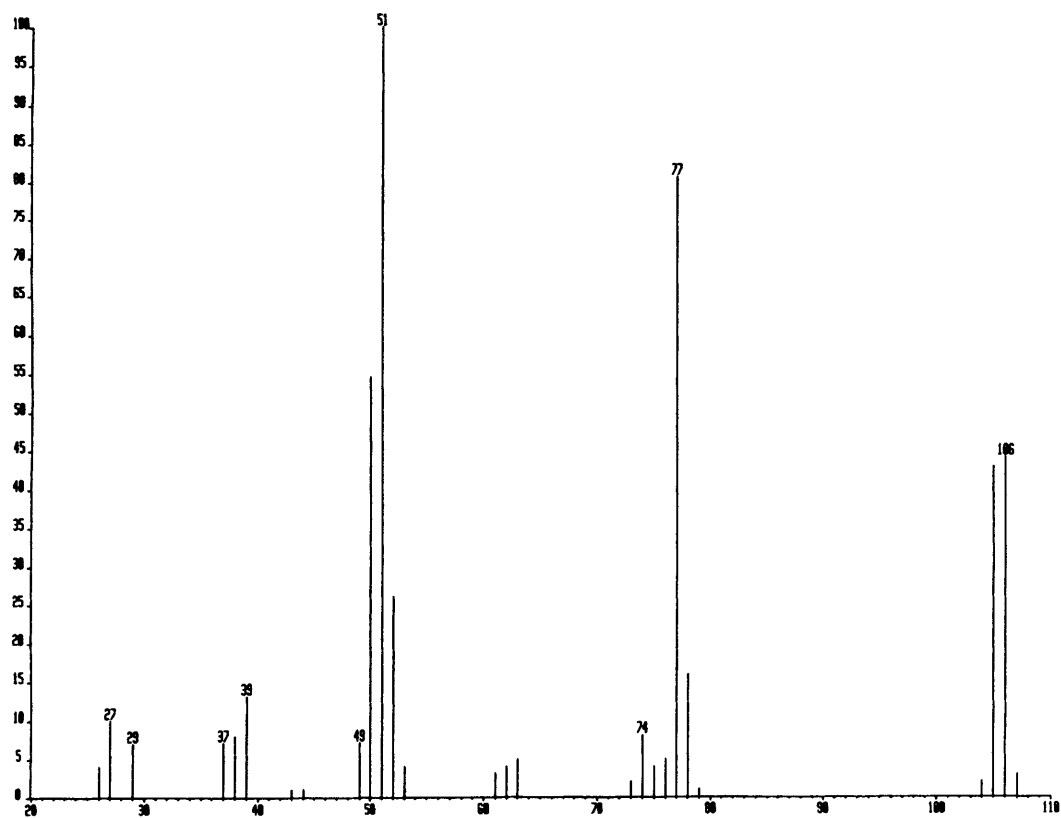
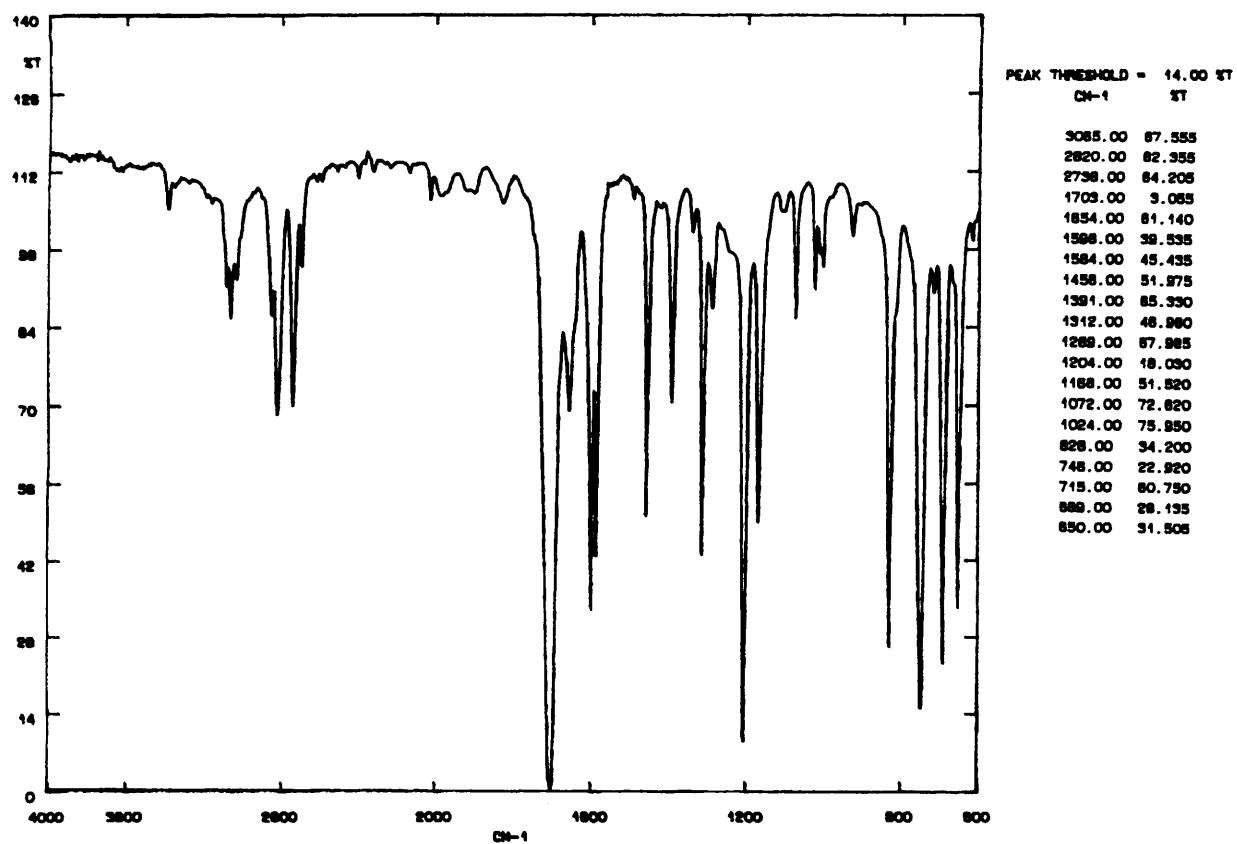
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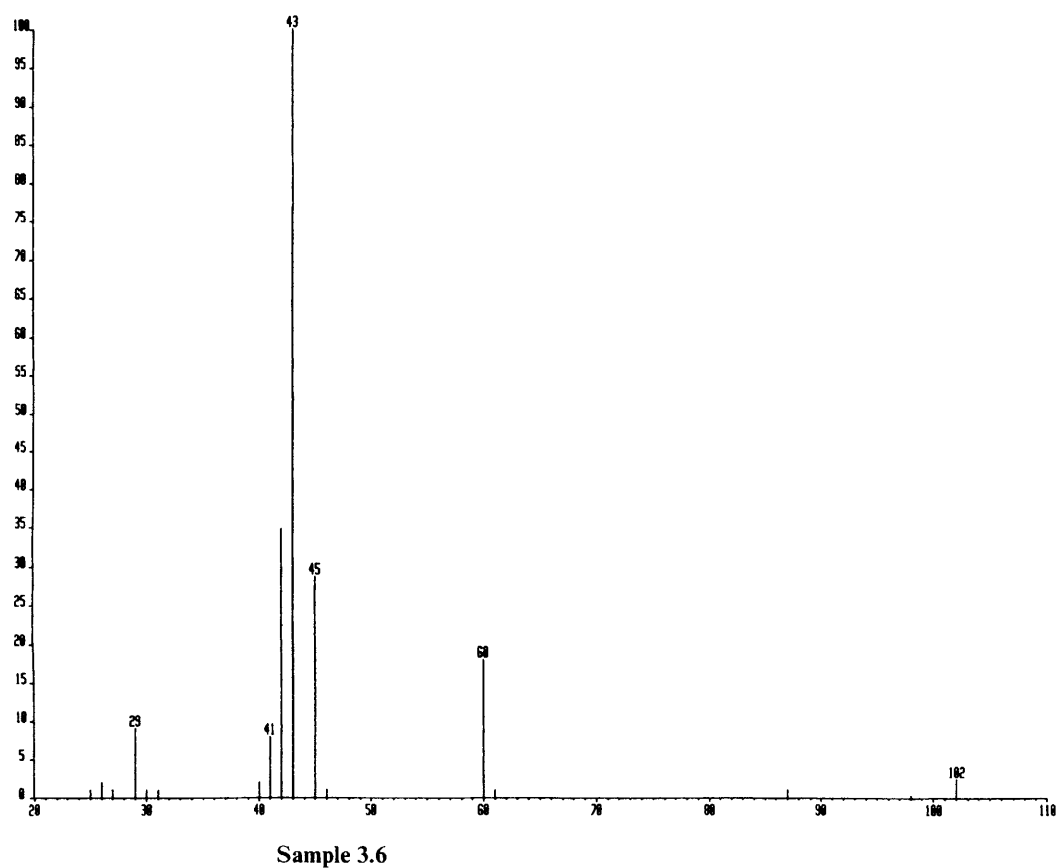
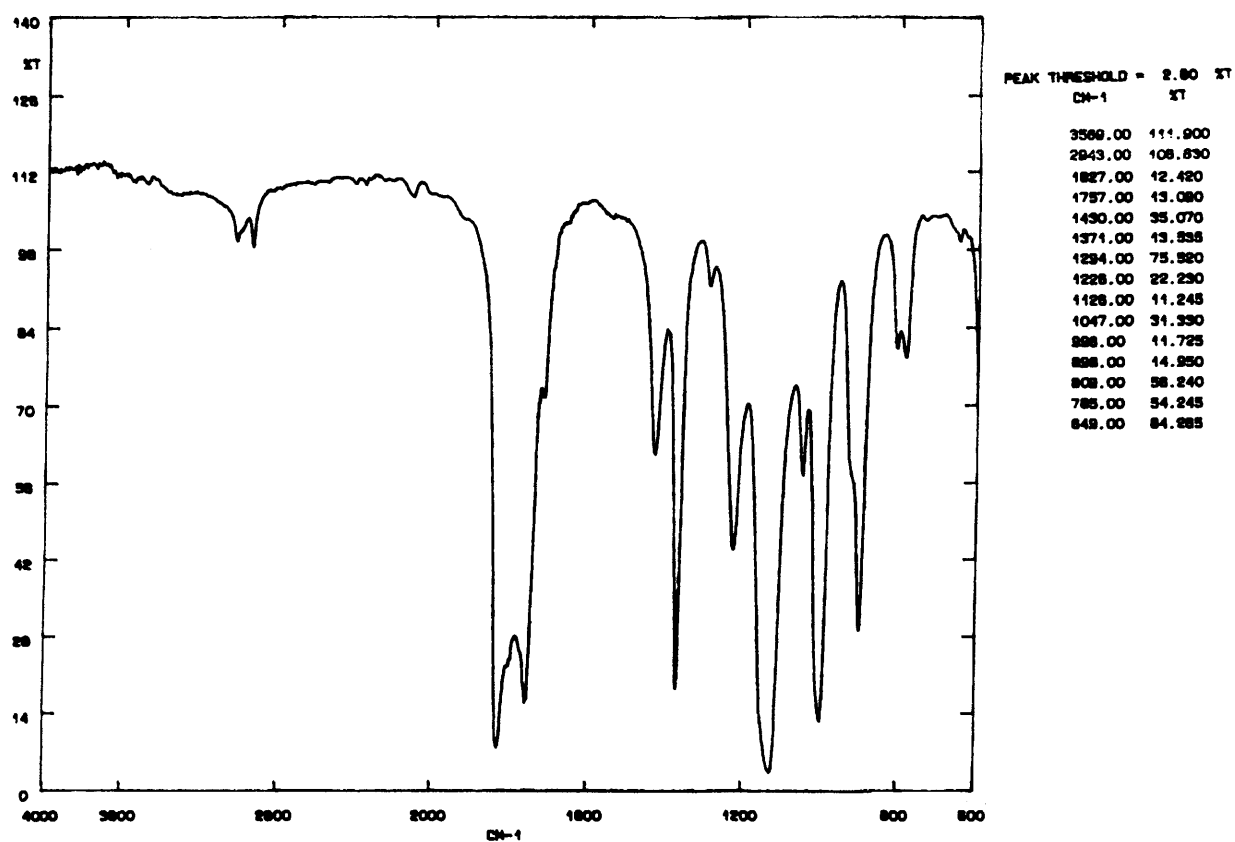
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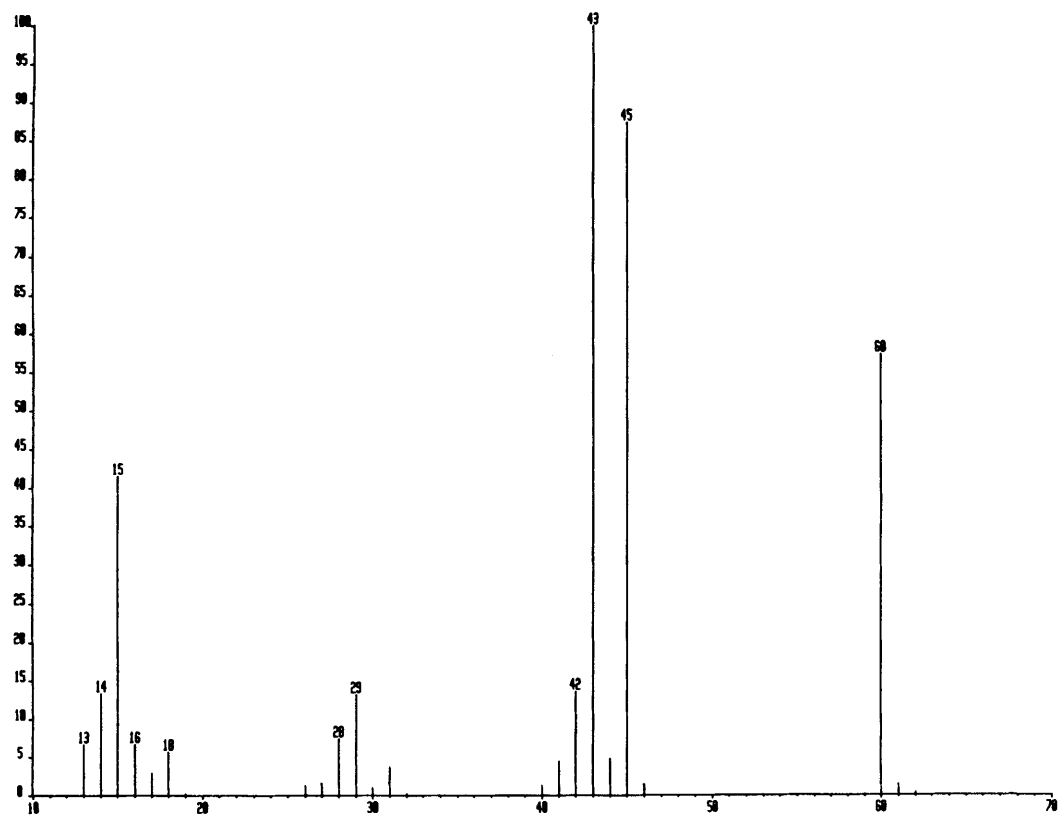
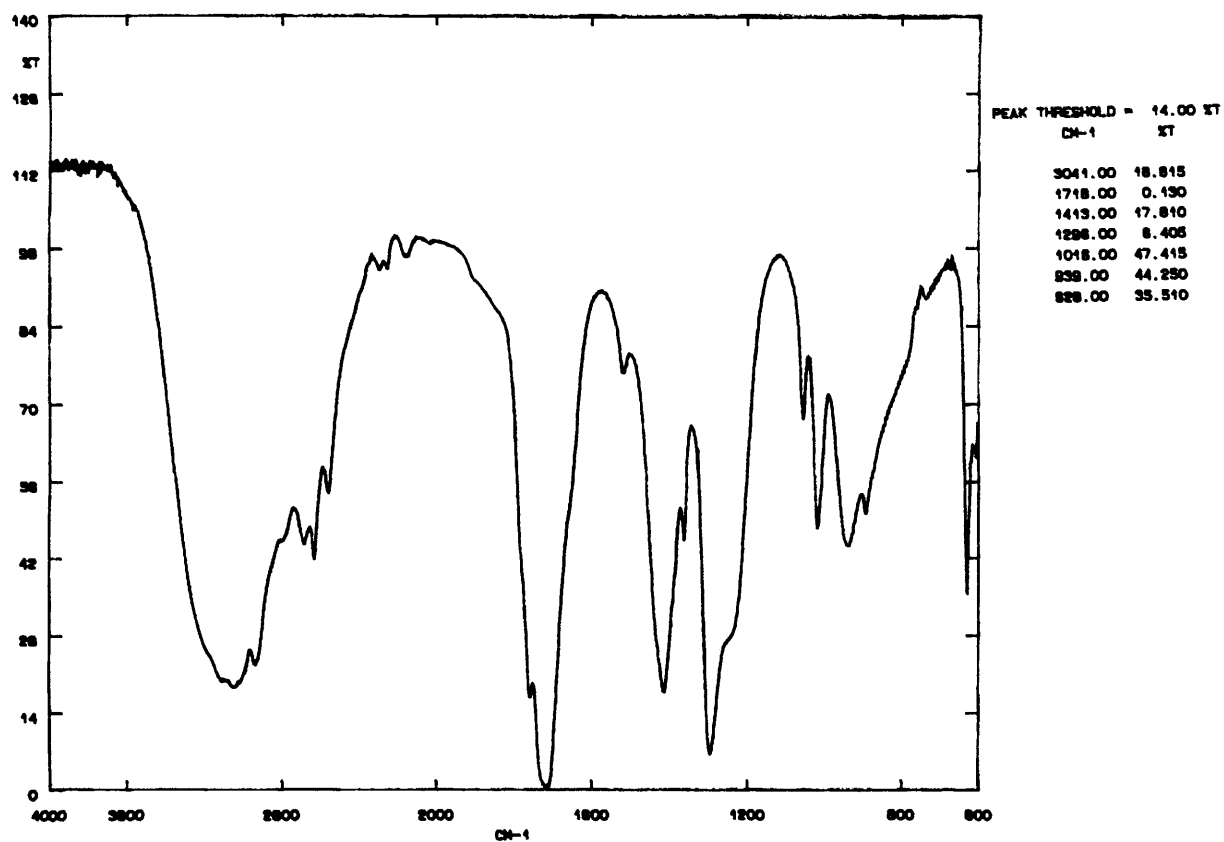


Sample 3.4



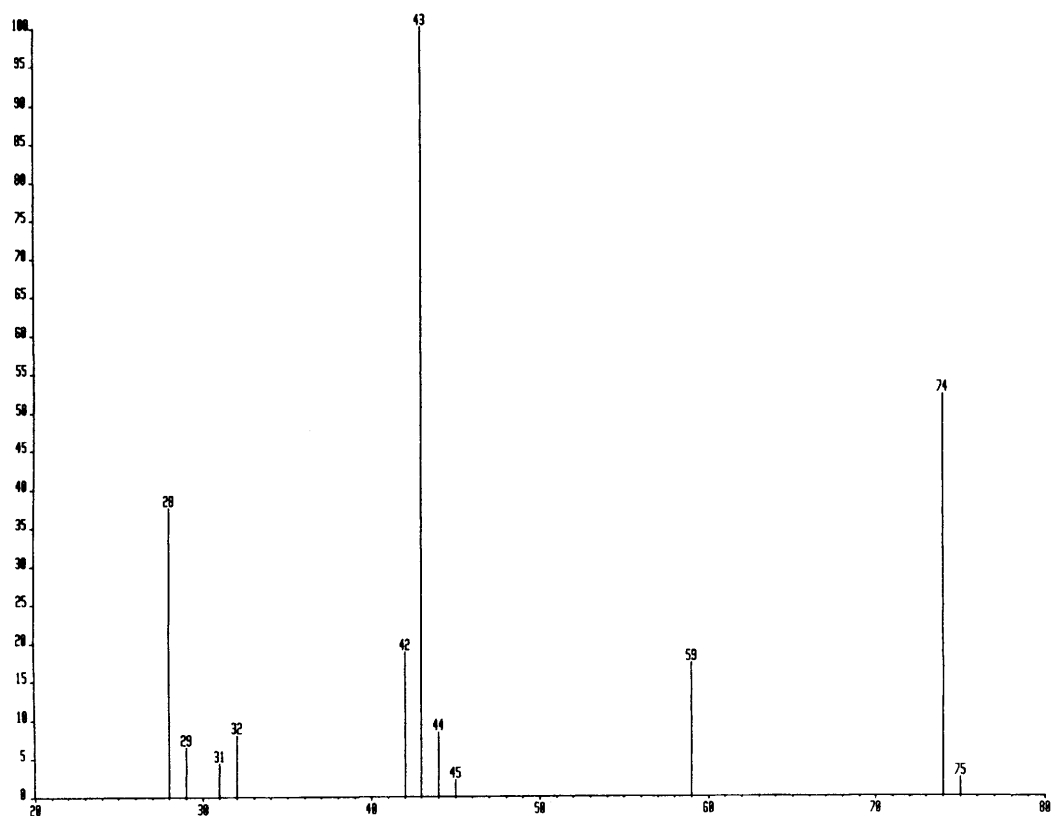
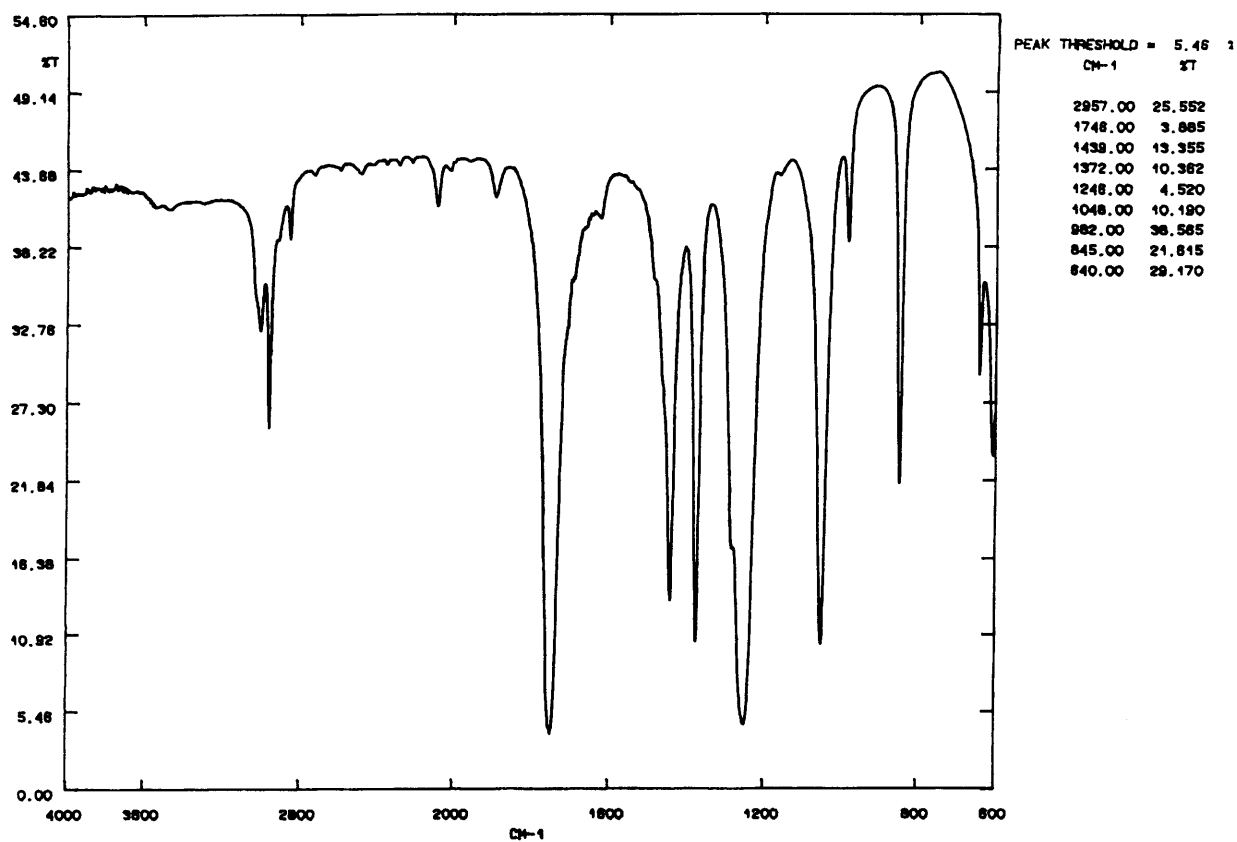
Sample 3.5



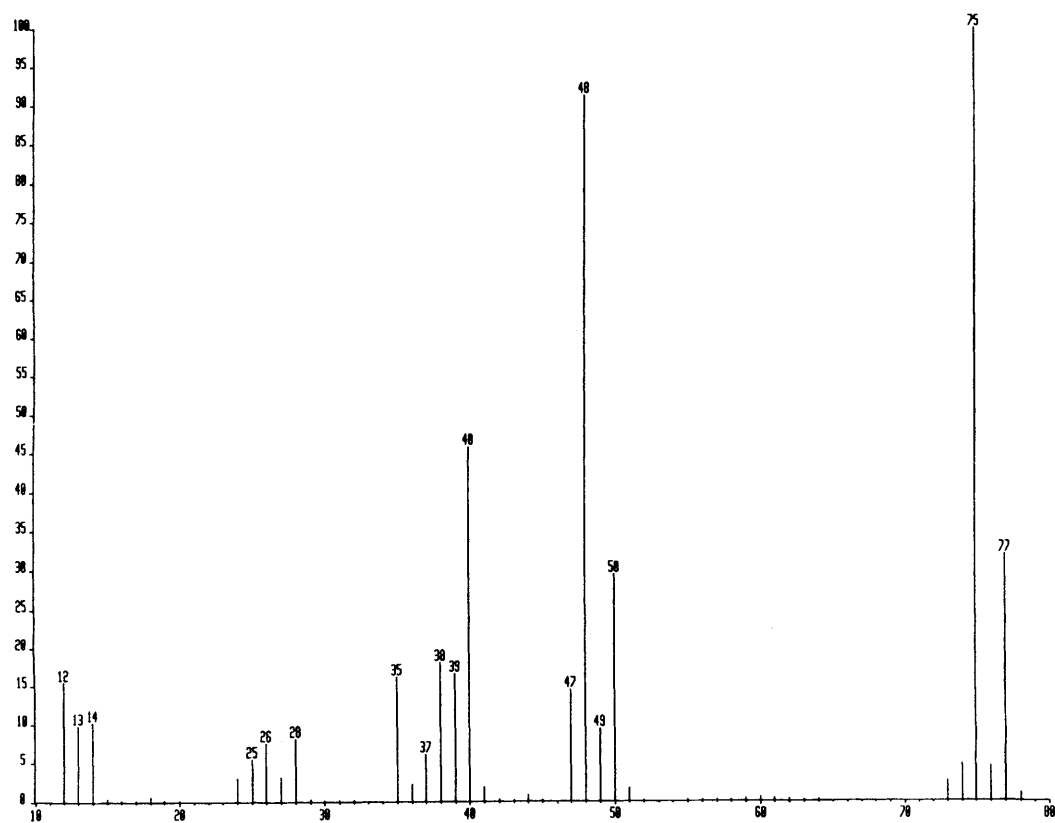
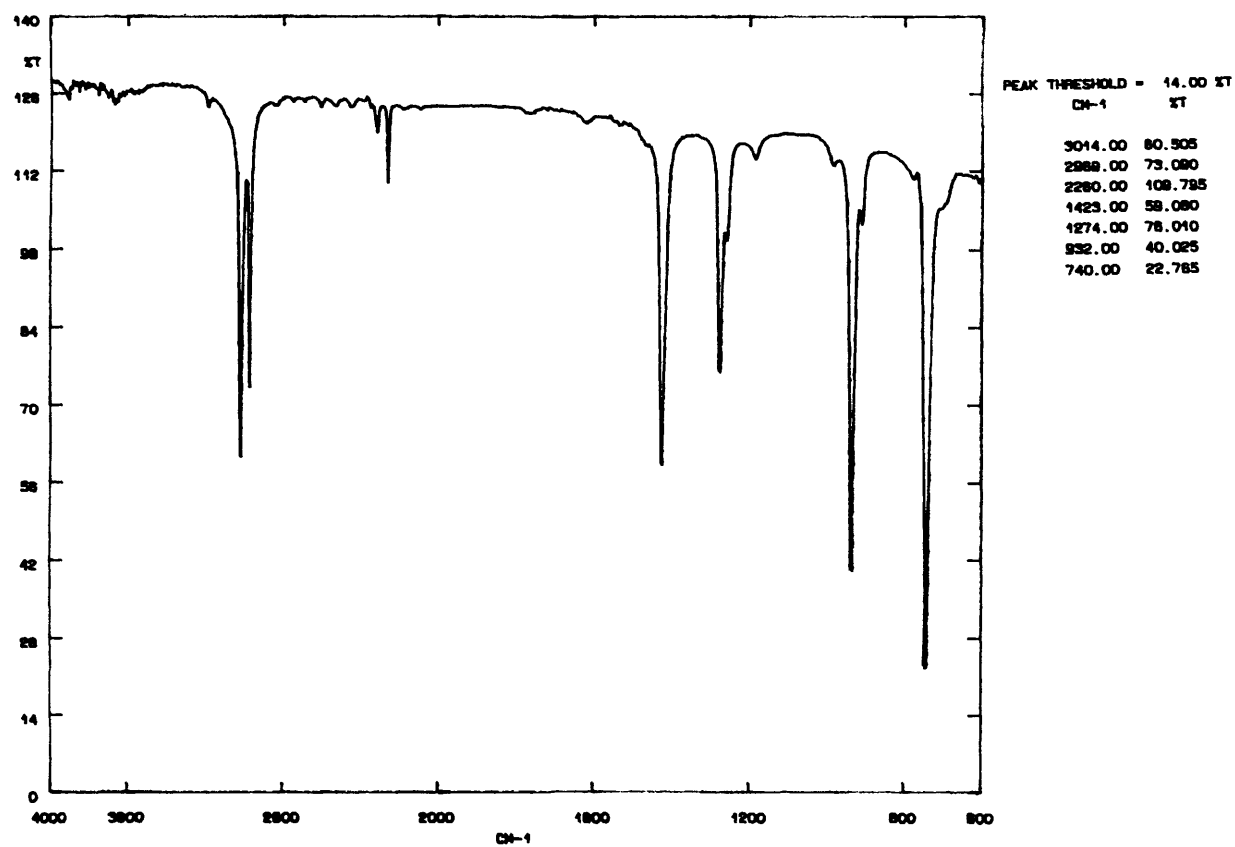


Sample 3.7

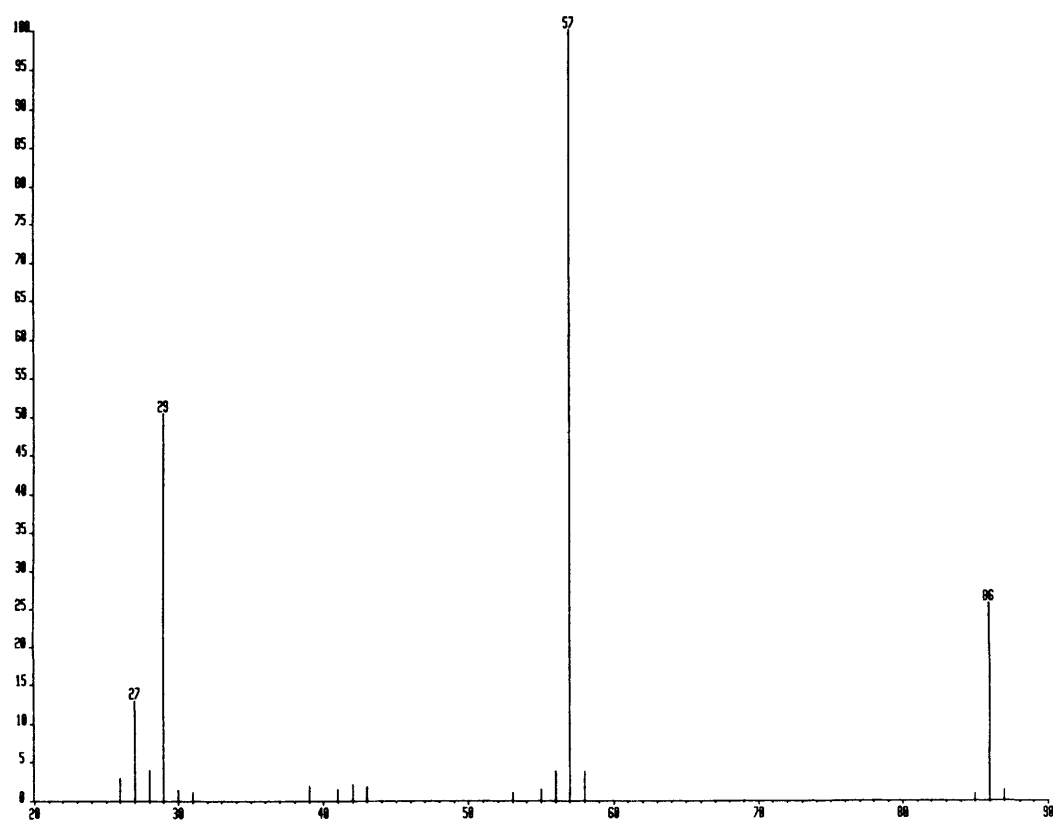
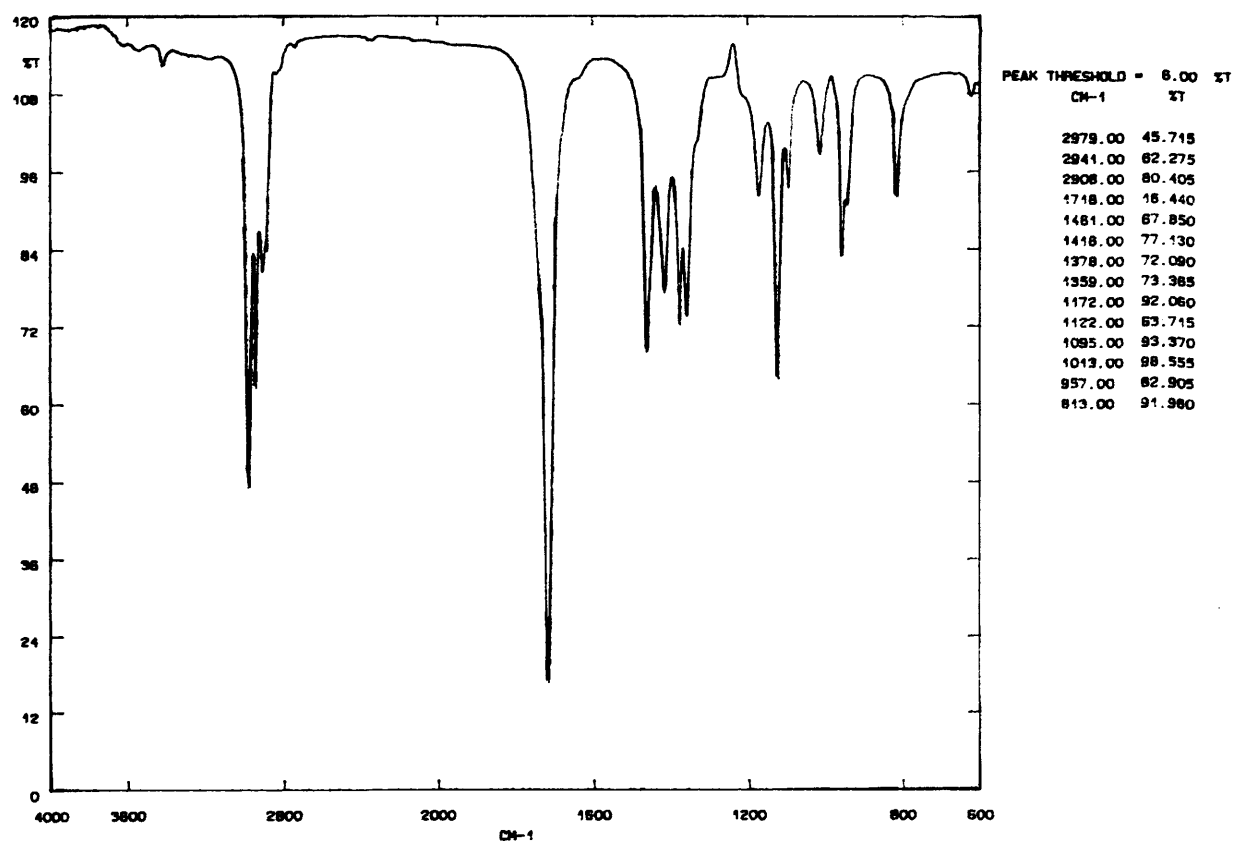




Sample 3.8



Sample 3.9



Sample 3.10

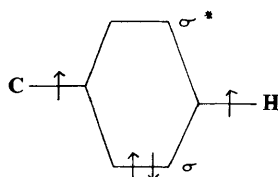


## Ultraviolet Spectroscopy

Ultraviolet spectroscopy tells us about conjugation in a molecule. It uses the highest energy radiation of any of the techniques described in this book; radiation at 200 nanometres is equivalent to 595 kilojoules per mole. Absorption of this energy raises an electron from a bonding orbital to an antibonding orbital.

Almost all ultraviolet spectroscopy involves radiation from 200 nm to 400 nm ( $1 \text{ nm} = 10^{-7} \text{ cm} = 10 \text{ \AA} = 1 \text{ m}\mu$ ). The region is often extended from 400 to 800 nm to cover the visible spectrum. The region below 200 nm, often referred to as the far ultraviolet, requires special equipment, since oxygen absorbs just below 200 nm.

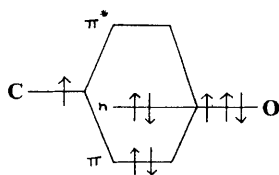
The ultraviolet spectrum measures the energy absorbed by an electron making the transition from a bonding to an antibonding orbital. If we look at a very simple molecule, methane,  $\text{CH}_4$ , then we see that it contains only C–H bonds. Since it is symmetrical, all the C–H bonds are equivalent, and we need to consider only one bond. If we take a carbon atom and a hydrogen atom, and consider a single electron attached to each, as shown in Diagram 4.1, we have the energy levels shown. If we then bring these atoms together, and use the electrons to form a bond, then two orbitals are formed, these having differing energy levels.



**Diagram 4.1** Orbital changes when a C atom and an H atom form a C–H bond

The bonding electrons occupy the lower level, known as the bonding orbital, denoted by  $\sigma$ . The upper orbital, known as the antibonding orbital and denoted by  $\sigma^*$ , is empty. When methane absorbs ultraviolet radiation, one of the bonding electrons can be raised to the antibonding orbital. The radiation at 140 nm has the right energy to make this transition occur. Consequently, methane does not absorb ultraviolet light between 200 and 400 nm. We can construct similar diagrams for C–C bonds, which have a  $\sigma \rightarrow \sigma^*$  transition at 150 nm, and C=C bonds, where the  $\pi \rightarrow \pi^*$  transition is at 170 nm.

When we consider a molecule which contains oxygen, we have to consider the effect of lone pairs of electrons, as well as  $\sigma$  and  $\pi$  bonding electrons. Thus, for the C=O bond of formaldehyde,  $\text{H}_2\text{C=O}$ , we can construct the diagram shown in Diagram 4.2. The  $n \rightarrow \pi^*$  transition results from the absorption of energy at 270 nm, so this transition is found in the ultraviolet spectroscopy range. It is the only transition not involving d orbitals found in the ultraviolet range, as the  $n \rightarrow \sigma^*$  (found in, for example, alcohols) absorbs radiation just above 200 nm.

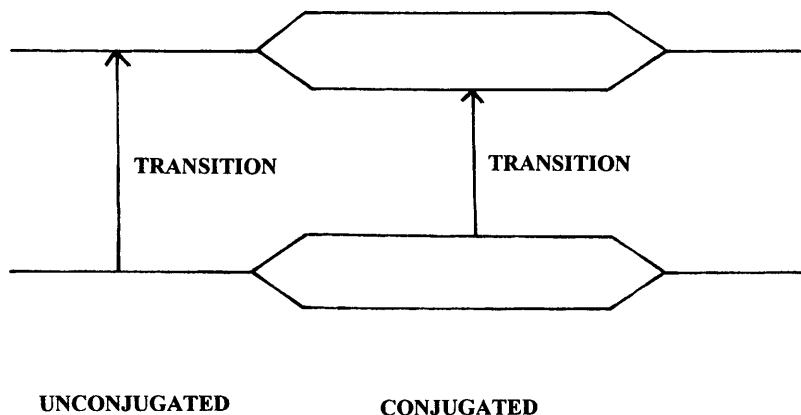


**Diagram 4.2** Orbital changes when a C atom and an O atom form a C=O bond

On this basis, ultraviolet spectroscopy would appear to be of limited value to organic chemists, since  $n \rightarrow \pi^*$  transitions are quite rare. However, we have to consider conjugation. If we have a molecule with two ultraviolet absorbing groups, which we call chromophores, the observed spectrum will be the simple sum of the absorptions due to the two chromophores, unless we have conjugation. If we do, then the energy of the highest bonding orbital is raised, and that of the lowest antibonding orbital is lowered, as shown in Diagram 4.3. Consequently, the energy difference between the levels is lowered and the transition takes place at lower energy, and absorbs radiation of longer wavelength. The more chromophores are involved in the conjugation, the greater the effect.

Molecule	Absorption
Ethylene	170 nm
Butadiene	217 nm
Hexatriene	253 nm

Double bonds can also absorb radiation above 200 nm as a result of conjugation with alkyne, ketone, aldehyde, ester, nitrile or amide groups.



**Diagram 4.3** Changes in transition energy resulting from changes in the energy of bonding and antibonding orbitals as a result of conjugation

The benzene ring, as might be expected, also absorbs ultraviolet radiation. Benzene itself absorbs at 184, 203.5 and 254 nm in hexane solution. The effect of conjugation with substituents is to move the absorption bands to longer wavelength. The band at 203.5 nm moves rapidly with increasing conjugation, and can overtake the band at 254 nm, which moves more slowly. The absorption can even move into the visible when we have an electron withdrawing and an electron attracting substituent in a 1,4- or *para*-substitution pattern, which is why compounds such as 1,4-nitrophenol are yellow.

A molecule which has absorbed ultraviolet radiation and been raised to an excited state can undergo many reactions which it would not undergo in the ground state. This field of chemistry is known as photochemistry. The excited state has a short lifetime, and usually undergoes decay by emitting its excess

energy. However, some energy is lost by collisions during the excited state, so the energy emitted is always less than that absorbed; radiation is consequently emitted at a longer wavelength. If we choose a molecule which absorbs radiation of a slightly shorter wavelength than visible light, then it will emit energy in the visible region when irradiated with ultraviolet radiation, and appear to be a pale blue colour. This phenomenon is known as fluorescence. It can be seen if a glass of tonic water (which contains quinine) is taken out of doors into the sunshine, when it appears to be a very pale blue. Compounds of this type are added to most washing powders: a white item washed in one of these will retain some of the fluorescing agent; it then reflects most of the light falling on it, but absorbs some ultraviolet radiation and emits it in the visible range, so that more visible radiation comes from the item than falls on it. It can then be described as 'whiter than white'. This can be demonstrated by shining an ultraviolet light on to a shirt washed in any washing powder. In a dark room, the shirt glows with a pale blue light. The experiment requires great care, as ultraviolet light can rapidly damage eyes, and can burn skin exposed to it.

Ultraviolet spectra are measured by dissolving the sample in a suitable solvent, often hexane or methanol, and scanning it, measuring absorption as a function of wavelength. Two pieces of information should be obtained about any absorption peak. The first is the wavelength of the peak maximum, denoted by  $\lambda_{\max}$ . The second is the intensity of the absorption. This depends on two laws, Lambert's law, which states that the fraction of the radiation absorbed is independent of the intensity of the radiation source, and Beer's law, which states that the absorption is proportional to the number of absorbing molecules. These laws lead to the equation

$$\log_{10} I_0/I = l c \epsilon$$

where  $I_0$  and  $I$  are the intensities of the incident and transmitted light, respectively,  $l$  is the path length of the cell in centimetres, and  $c$  is the concentration of the solution of the sample in moles per litre. The remaining factor,  $\epsilon$ , is called the molar extinction coefficient for the particular peak of the compound being studied. By convention, it is always given without units (the actual units are  $1000 \text{ cm}^2 \text{ mol}^{-1}$ ). The value of  $I_0/I$  is called the absorbance or optical density, and most spectrometers draw the spectrum as a graph of  $\log_{10} I_0/I$  as a function of wavelength.

The value of  $\epsilon_{\max}$  (the molar extinction coefficient at the peak maximum) is useful because it tells us if the transition we are interested in is 'allowed' or 'forbidden'. Transitions are 'forbidden' for complex reasons of symmetry, but actually occur weakly because the symmetry which makes them forbidden is broken by molecular vibrations or by substitution. As an approximate rule, forbidden transitions have  $\epsilon_{\max}$  values below about 1000, usually well below. The  $n \rightarrow \pi^*$  transition in ketones is an example of a forbidden transition, in which  $\epsilon_{\max}$  values are usually below 100. In contrast,  $\pi \rightarrow \pi^*$  transitions are allowed, and  $\epsilon_{\max}$  is usually above 1000. Conjugation usually increases the value of  $\epsilon_{\max}$ .

Let us now look at an ultraviolet spectrum, shown in Figure 4.1. The spectrum is that of a saturated ketone, butan-2-one,  $\text{CH}_3\text{COCH}_2\text{CH}_3$ . The spectrum shows a single absorption peak at  $\lambda_{\max}$  279 nm,  $\epsilon_{\max}$  16.6. This very low value of  $\epsilon_{\max}$  shows us that this is a forbidden transition, an  $n \rightarrow \pi^*$  transition, characteristic of an aldehyde or ketone group or a nitro group. These peaks all occur within the general range of 275–290 nm. Note that

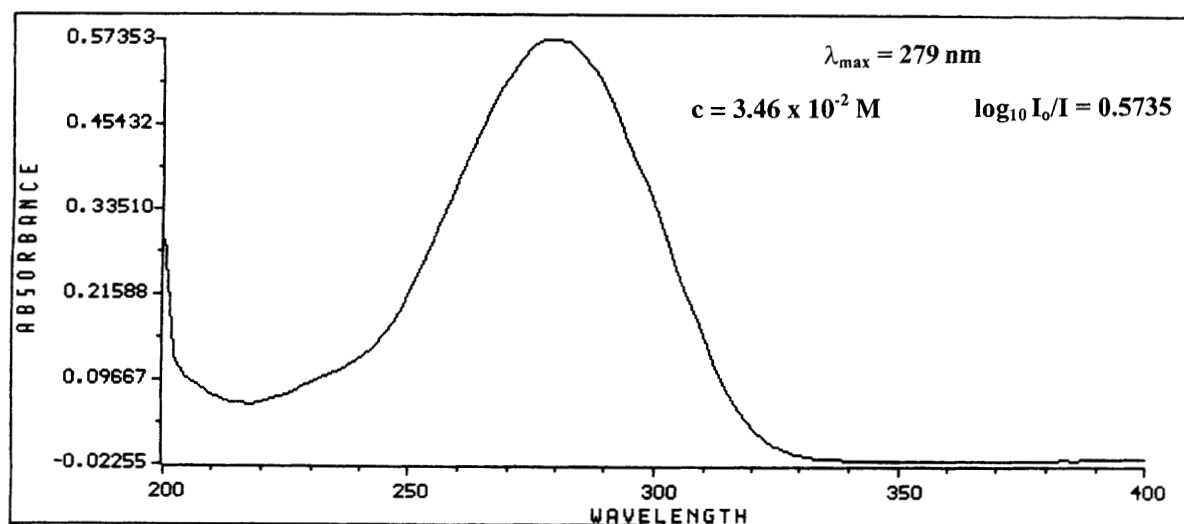


Figure 4.1

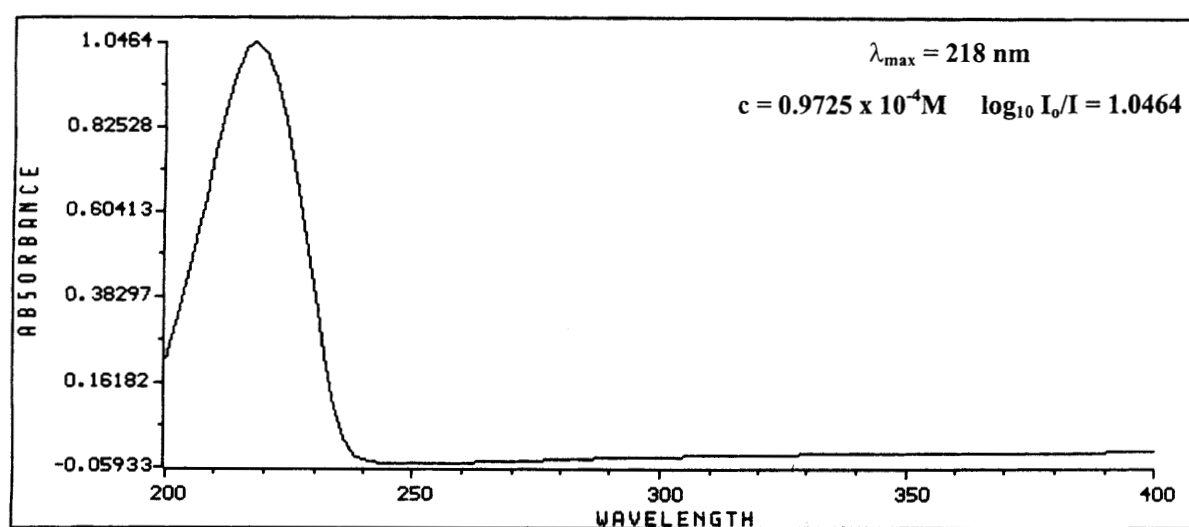


Figure 4.2

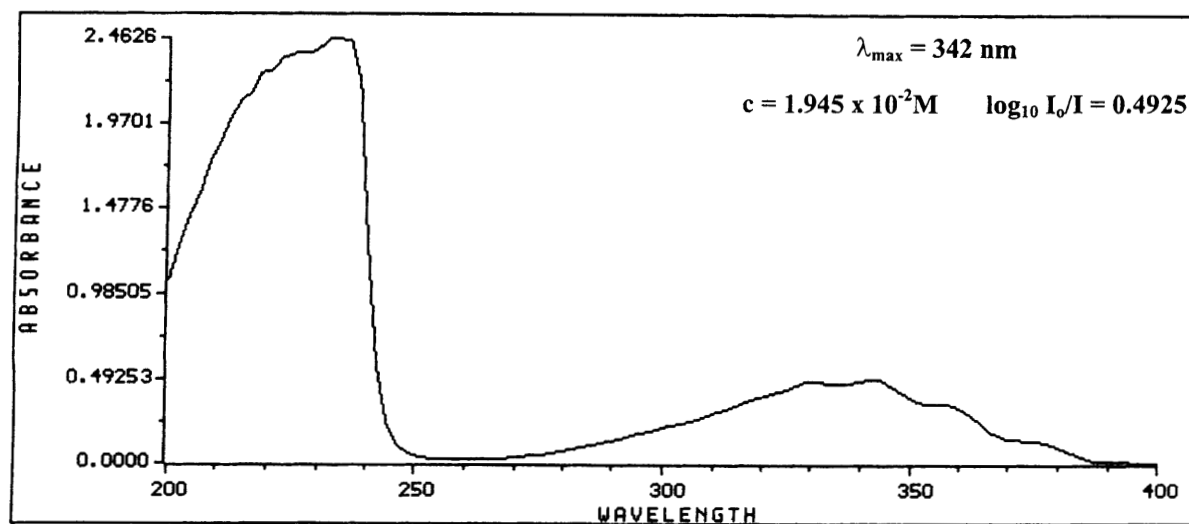


Figure 4.3



esters, acids and amides do not show this absorption; they absorb in the 200–215 nm region.

The next spectrum is that of an  $\alpha,\beta$ -unsaturated ketone, cyclohexanone. The spectrum has two absorption peaks, of such widely differing  $\epsilon_{\max}$  values that they have to be recorded at different concentrations. The spectra obtained are shown in Figures 4.2 and 4.3. The more intense absorption is shown in Figure 4.2 which shows a peak at  $\lambda_{\max} = 218$ , with  $\epsilon_{\max} = 10\,760$ . This is clearly not a forbidden transition, so must be the  $\pi \rightarrow \pi^*$  transition moved to longer wavelength by conjugation. The weaker absorption is shown in Figure 4.3. The region around 200–250 nm is swamped by the intense absorption of the  $\pi \rightarrow \pi^*$  transition, but the spectrum shows a peak at  $\lambda_{\max} = 342$  nm,  $\epsilon_{\max} = 25.3$ . The low intensity of this peak shows it to be a forbidden transition, an  $n \rightarrow \pi^*$  transition. It is at higher wavelength than the previous  $n \rightarrow \pi^*$  transition and has slightly higher  $\epsilon_{\max}$  as a result of conjugation with the  $\pi \rightarrow \pi^*$  transition. Conjugated  $n \rightarrow \pi^*$  carbonyl peaks usually occur in the 300–350 nm region, and have  $\epsilon_{\max}$  below 100. Clearly, we have a double bond conjugated with a carbonyl group.

### Summary

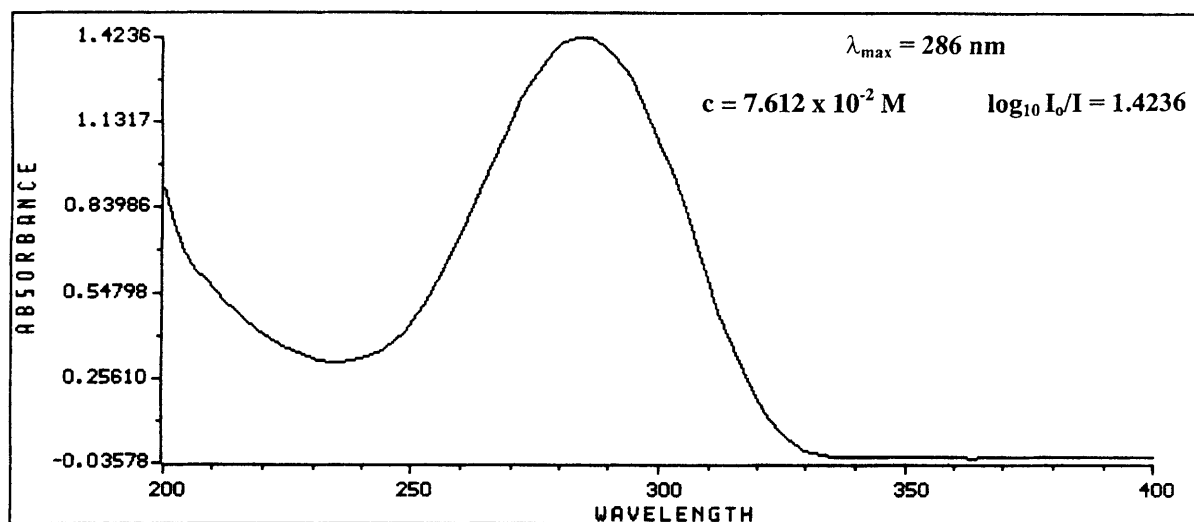
The first thing to do with an ultraviolet spectrum is to observe the values of  $\lambda_{\max}$  and  $\log_{10} I_0/I$  at  $\lambda_{\max}$ , and hence calculate  $\epsilon_{\max}$ .

Then, if  $\epsilon_{\max}$  is over about 1000, we have an allowed transition, usually  $\pi \rightarrow \pi^*$ , and the value of  $\lambda_{\max}$  gives some idea as to the amount of conjugation involved. The exact position of the peak can provide a lot of information about the conjugated system, using a complex set of rules known as Woodward's rules.

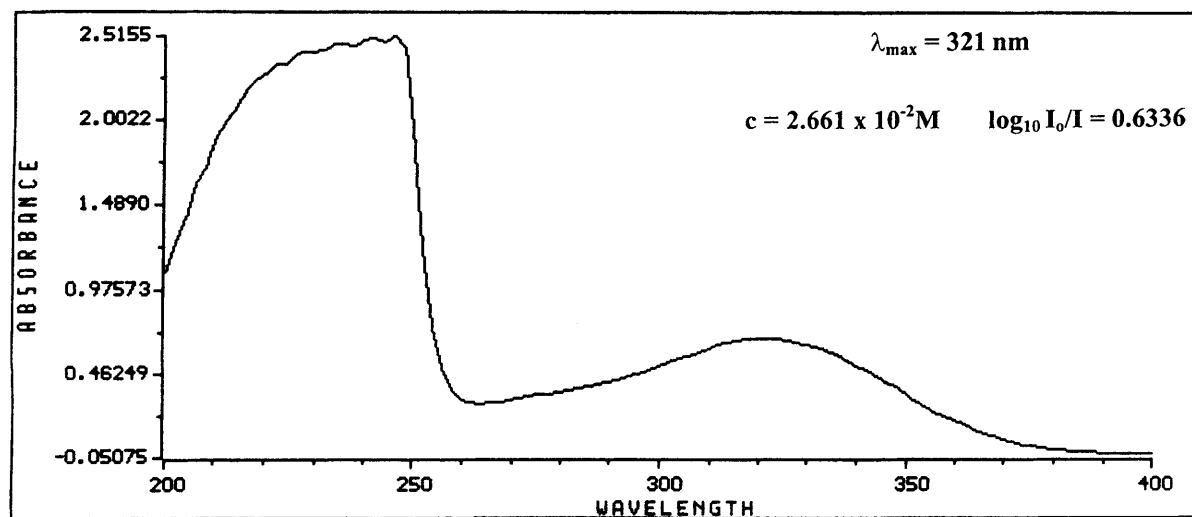
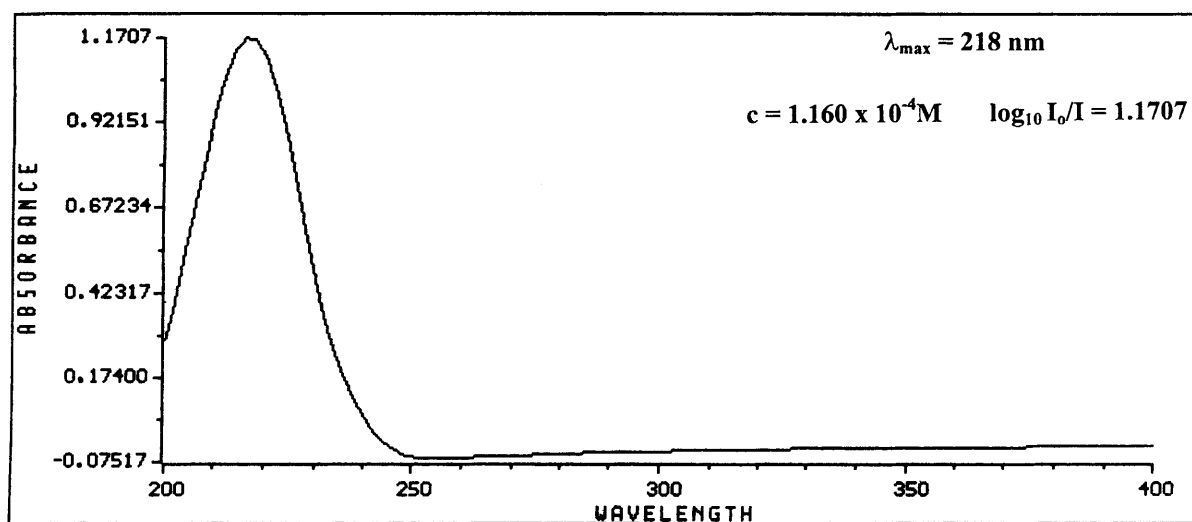
If  $\epsilon_{\max}$  is below about 1000, then we have a forbidden transition, usually  $n \rightarrow \pi^*$ . Peaks in the range 275–295 nm are not conjugated; peaks in the range 300–350 nm are conjugated to a  $\pi \rightarrow \pi^*$  transition. Conjugation of two carbonyl peaks can occur in dicarbonyl compounds, and leads to two  $n \rightarrow \pi^*$  transitions at 290 nm and 340–440 nm, which is why some of these compounds are yellow.

### Problems in Interpreting Ultraviolet Spectra

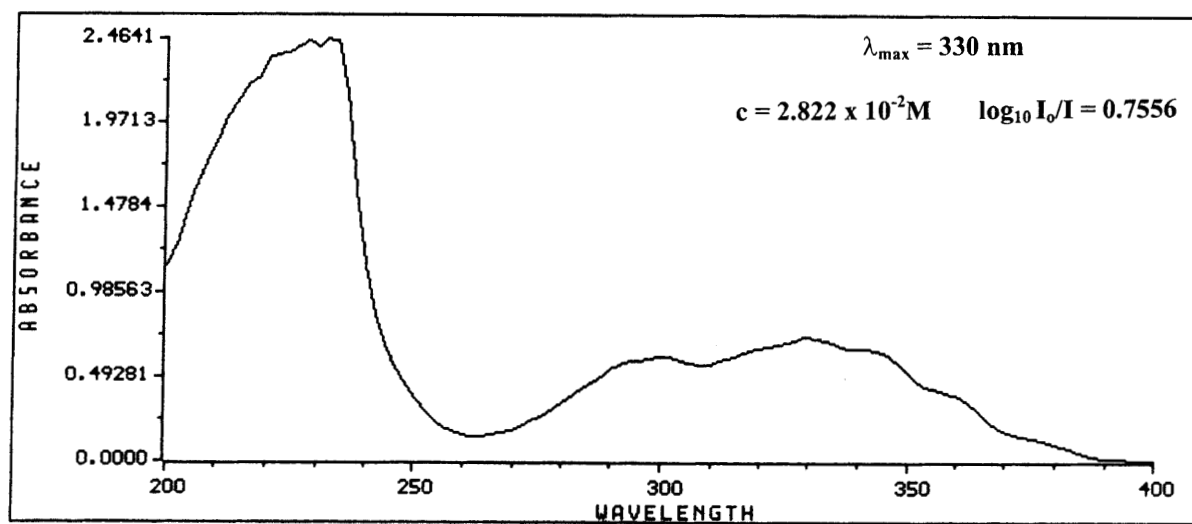
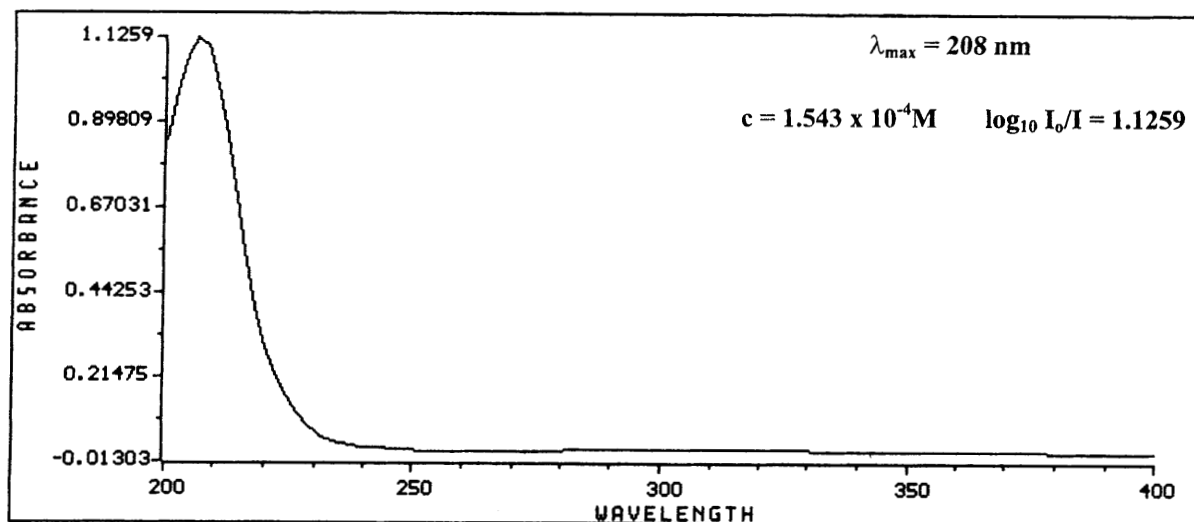
You are given the ultraviolet spectra of five samples. Calculate the  $\epsilon_{\max}$  value of each peak, and hence decide if the peak is  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$ . Use the  $\lambda_{\max}$  values to decide if either the  $\pi \rightarrow \pi^*$  or the  $n \rightarrow \pi^*$  transition involves a conjugated system. Hence, suggest the type of structure, *e.g.* diene or ketone or  $\alpha,\beta$ -unsaturated ketone, present in the sample.



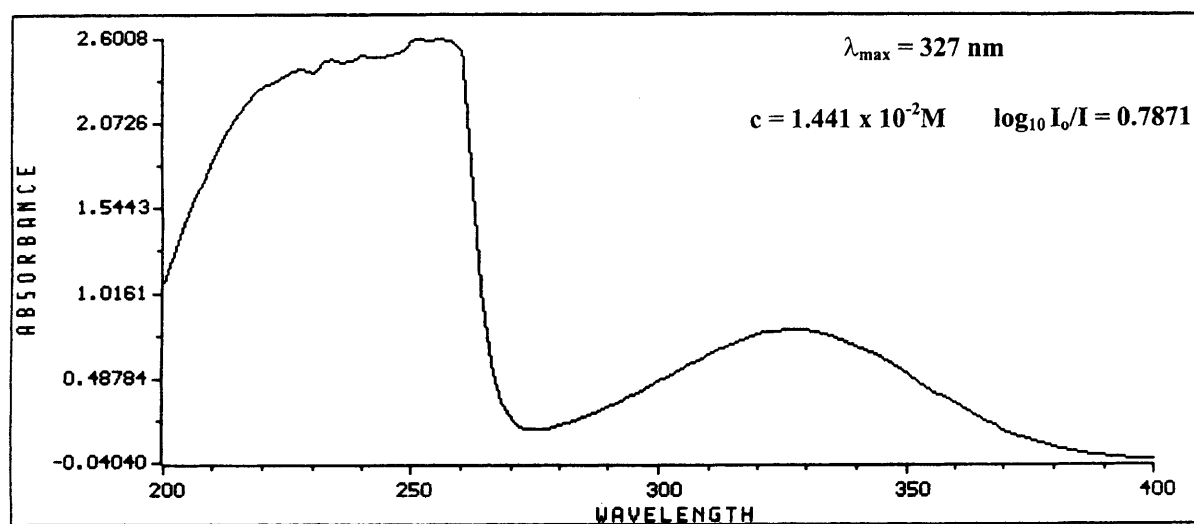
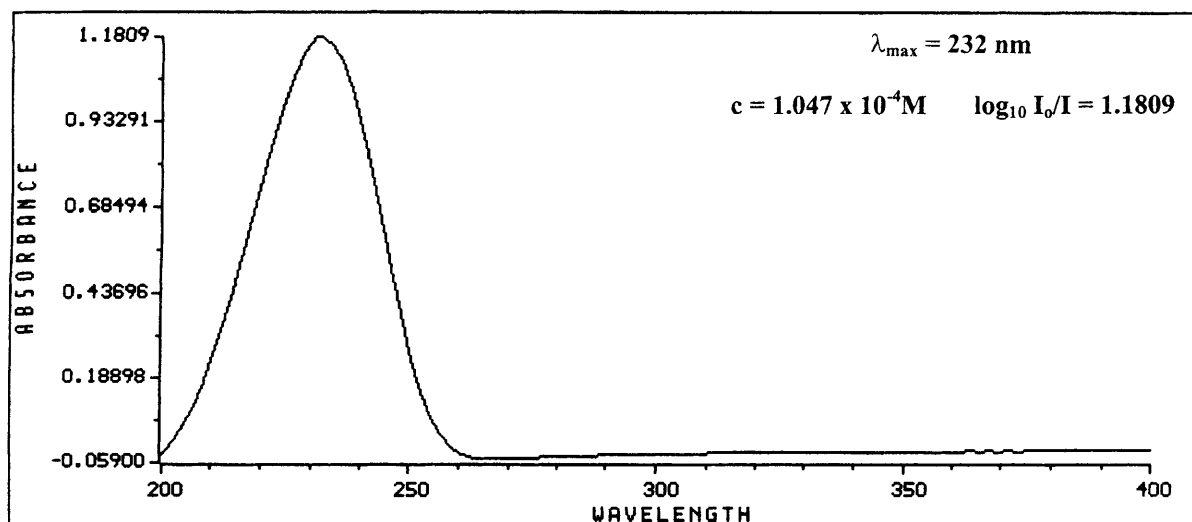
Sample 4.1



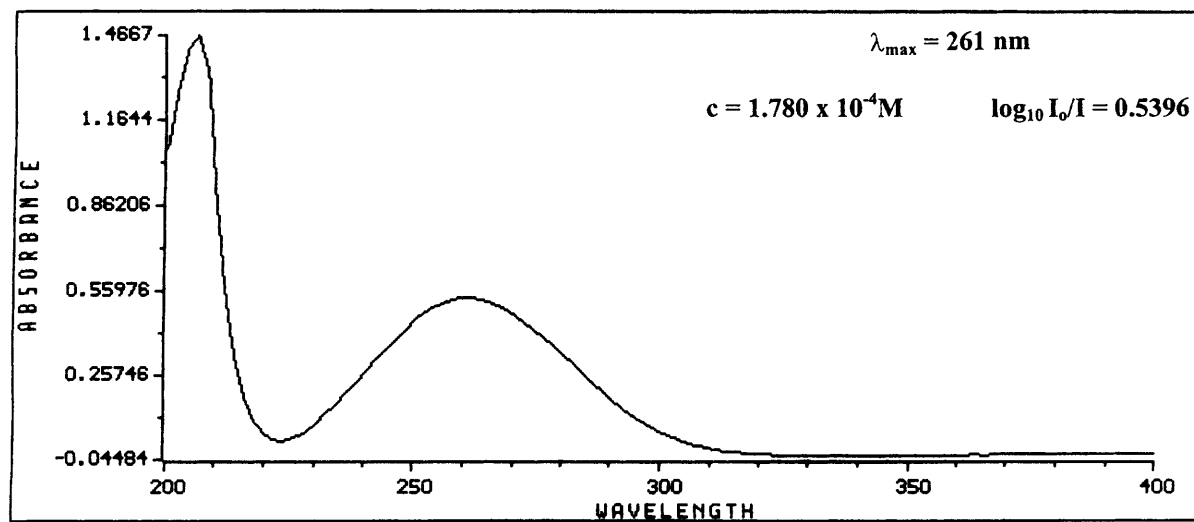
Sample 4.2



Sample 4.3



Sample 4.4



Sample 4.5

## **$^{13}\text{C}$ Nuclear Magnetic Resonance Spectroscopy**

$^{13}\text{C}$  NMR spectroscopy tells us about the environments of the carbon atoms in a molecule. The technique of NMR can be applied only to atoms which have nuclear spin; when they are placed in a strong magnetic field, the nuclear spins can take up different orientations which are at different energy levels. For nuclei with nuclear spin of  $\frac{1}{2}$ , such as  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$ , the nuclei orient themselves in one of two ways\*. When the nucleus is irradiated with radiation of the appropriate frequency (radiofrequency), some of the nuclei in the lower energy state absorb radiation and are raised to the higher energy state. When irradiation stops, they relax to the equilibrium distribution. This relaxation process is quite slow.

The frequency of the radiation absorbed depends on the magnetic field applied to the nucleus. The field is normally made up of three components:

- A. The externally applied field. This is an extremely powerful magnetic field. When a field of 23.49 kilogauss is applied to a carbon nucleus, it absorbs radiation at 25.14 MHz. The same field, applied to a hydrogen nucleus, would make it absorb radiation at 100 MHz. Since most machines run  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra, the radiation absorbed by the latter is often used to describe the power of the machine. Thus, a machine with a field of 23.49 kilogauss would be described as a 100 MHz spectrometer. To attain high, stable magnetic fields, superconducting magnets, kept at the temperature of liquid helium, are often used. The externally applied field is responsible for almost all the magnetic field applied to the nucleus, but the field is slightly modified by the effects of neighbouring atoms. If this did not happen, all carbon atoms would absorb radiation at the same frequency.
- B. The applied field can be affected by the variation in electron density around the neighbouring nuclei. Movement of these electrons in the applied field creates a magnetic field which opposes the applied field, hence changing the absorption frequency. Since hydrogen is (almost) the least electronegative element, replacement of a hydrogen on a carbon atom by any other atom moves the absorption frequency of that carbon atom to that associated with a lower magnetic field, usually described as downfield. This movement is referred to as chemical shift, and it is always proportional to the applied field.
- C. The applied field is affected by the field resulting from the nuclear spin of neighbouring nuclei. These can be aligned with or against the applied field, either increasing or decreasing it. Consequently, a nucleus having one neighbouring atom with nuclear spin has an equal chance of being

\*They are often pictured as being like small bar magnets, and aligning themselves with or against the magnetic field—a useful, though simplistic, illustration.

in a field increased or decreased by that neighbouring atom, and hence the absorption peak is split into two equal peaks. This interaction of nuclei, described as coupling, results directly from the magnetic field of the nucleus, so is not influenced by the strength of the applied field.

For any nucleus, the frequency of the radiation absorbed depends on the magnetic field, so that we have two variables to consider when constructing a scale. It is difficult to measure very high magnetic fields with the degree of accuracy required to produce an absolute scale, so absorption frequencies are measured as the frequency in Hertz from an arbitrary standard. In  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy this standard is tetramethylsilane [TMS,  $\text{Si}(\text{CH}_3)_4$ ], which absorbs upfield of most carbon and hydrogen atoms. The position of absorption of any peak depends on the applied field, so that an absorption peak which is at 50 Hz from TMS in a 100 MHz spectrometer will be at 100 Hz from TMS in a 200 MHz spectrometer. We therefore measure absorption frequencies on the  $\delta$  scale, defining  $\delta$  as:

$$\delta = \frac{\text{Shift in Hz from TMS}}{\text{Operating frequency in MHz}}$$

Thus, in our example

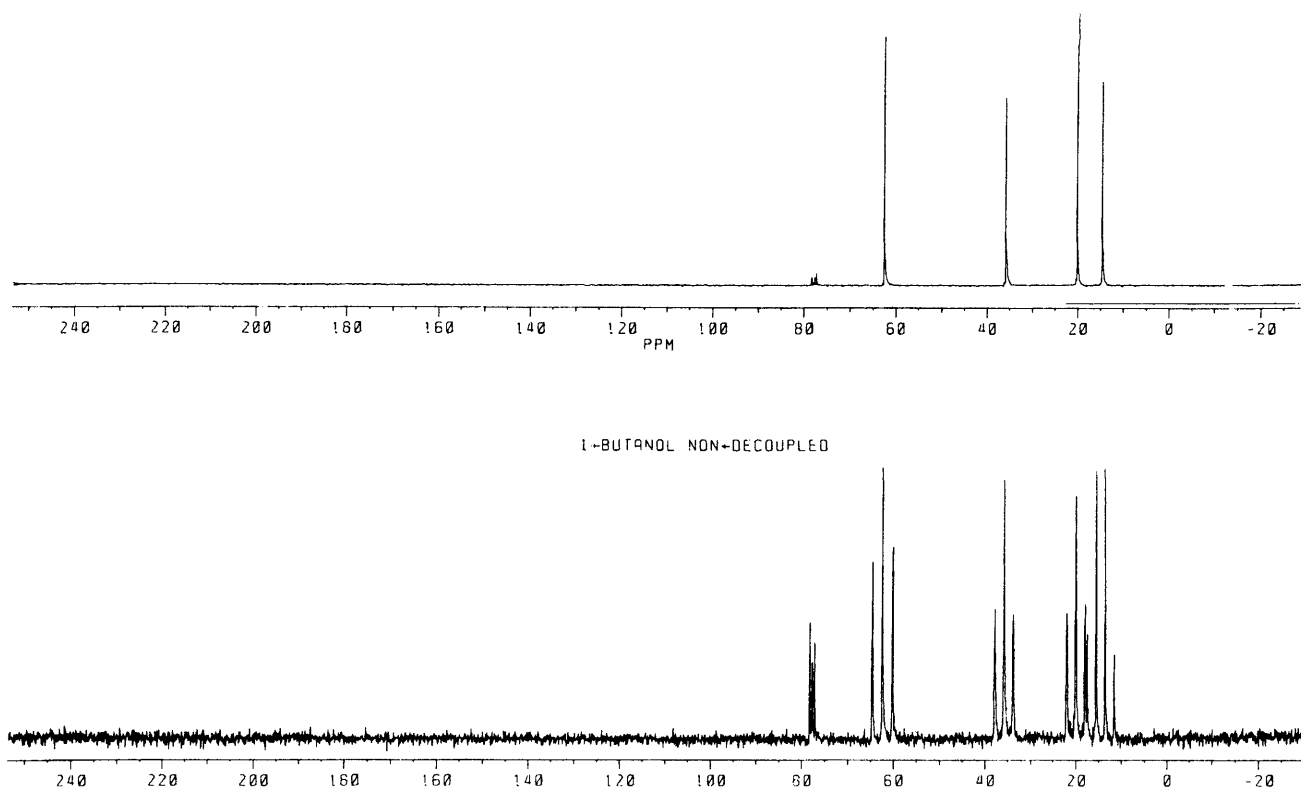
$$\delta = \frac{50}{100} = \frac{100}{200} = 0.5$$

The value of  $\delta$  has no units, and is expressed as fractions of the applied field in parts per million (ppm).

To measure a  $^{13}\text{C}$  NMR spectrum, we place a solution of the compound being studied in a magnetic field, spin it to even out the effect of any variations in the field, then irradiate it and measure the absorption of radiation as a function of the frequency of radiation.

The permanent problem of  $^{13}\text{C}$  NMR spectroscopy is that natural carbon is only 1.1%  $^{13}\text{C}$ . Thus, even a pure liquid is only a dilute solution of the material which is giving a spectrum, and background electronic noise levels are high. One possible approach would be to scan the spectrum repeatedly and accumulate the spectra on top of each other, so that electronic noise cancelled out, and the spectrum emerged. This process would be extremely slow, since each scan takes about five minutes. The problem has been solved by using rapidly repeated scans with a single powerful pulse covering the whole frequency range. This can be repeated until a sufficiently strong spectrum is obtained, which is then transformed into the spectrum obtained from a conventional scan by a Fourier transform. The method is highly efficient, but has one major snag. Since the sample is scanned many times in rapid succession, not all nuclei have time to revert to their equilibrium distribution of nuclear spin states before the next burst of scanning radiation comes along. Consequently the nuclei with longer relaxation times, which are not fully relaxed, absorb less energy from the second and subsequent bursts of radiation than do those nuclei which are fully relaxed. As a result, the absorption band in the final spectrum from an atom with a long relaxation time, such as a carbonyl or quaternary carbon atom, is smaller than the absorption band from an atom with a shorter relaxation time. As a result, in a Fourier Transform (FT) spectrum, we cannot use peak areas as a measure of the number of nuclei in a particular environment.

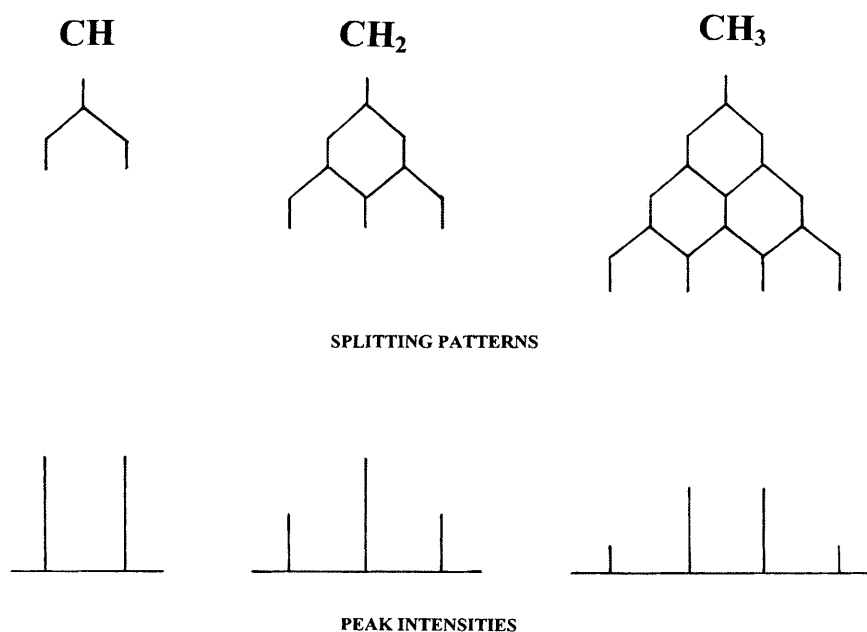
We can, however, make good use of this phenomenon. Most NMR spectra are measured in solution. We need a solvent which, ideally, does not contain

**Figure 5.1**

any carbon atoms. This is not practical in  $^{13}\text{C}$  NMR work, but if we choose a solvent in which the carbon atoms have a deuterium substituent, then that solvent will have a very weak  $^{13}\text{C}$  absorption spectrum because a deuterium substituent greatly lengthens the relaxation time of a carbon atom. We choose  $\text{CDCl}_3$  for most purposes. Since the deuterium nucleus has a spin of 1, it splits the carbon peak into three equal peaks, so our solvent gives three relatively weak peaks around  $\delta 77$ .

An example of a  $^{13}\text{C}$  NMR spectrum is shown in Figure 5.1. It shows the  $^{13}\text{C}$  NMR spectrum of butan-1-ol,  $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--OH}$ . The figure shows two traces. The upper is known as the decoupled spectrum, and shows one line for each carbon atom in a different environment. In this case, there are four lines, since all the four carbon atoms are in different environments, and hence have different chemical shifts. The lower trace shows the uncoupled spectrum, in which each of these peaks is split into a multiplet by the attached hydrogen atoms.

We have already seen that the absorption band from an atom is split into two bands by the magnetic field of a neighbouring nucleus with nuclear spin. This is not a problem with  $^{13}\text{C}$  to  $^{13}\text{C}$  interaction, since  $^{13}\text{C}$  is present to only 1.1%, so any  $^{13}\text{C}$  atom is likely to have only  $^{12}\text{C}$  neighbours, which do not have nuclear spin. The small amount of splitting from  $^{13}\text{C}$  to  $^{13}\text{C}$  coupling would be lost in the electronic noise. However, the signal from any  $^{13}\text{C}$  atom with a  $^1\text{H}$  atom would be split by the magnetic field of that atom. In order to obtain the upper trace, we observe the  $^{13}\text{C}$  absorption while strongly irradiating the sample with radiation absorbed by  $^1\text{H}$  atoms. This causes the  $^1\text{H}$  atoms to flip very rapidly between spin states several times while the  $^{13}\text{C}$  signal is being recorded. The  $^{13}\text{C}$  atom thus experiences an averaged spin system from the neighbouring  $^1\text{H}$  nucleus, and is not split. This process is referred to as decoupling, and the  $^{13}\text{C}$  spectrum recorded under these conditions is called a decoupled spectrum.



**Diagram 5.1** Splitting patterns and peak intensities for the spectra of carbon atoms bearing hydrogen atoms

If we then turn the irradiation off, then the carbon signals are split by the effects of the hydrogen atoms, and we get the lower trace shown in Figure 5.1. This shows the  $^{13}\text{C}$  to  $^1\text{H}$  splitting, and enables us to say how many hydrogen atoms are attached to each carbon atom.

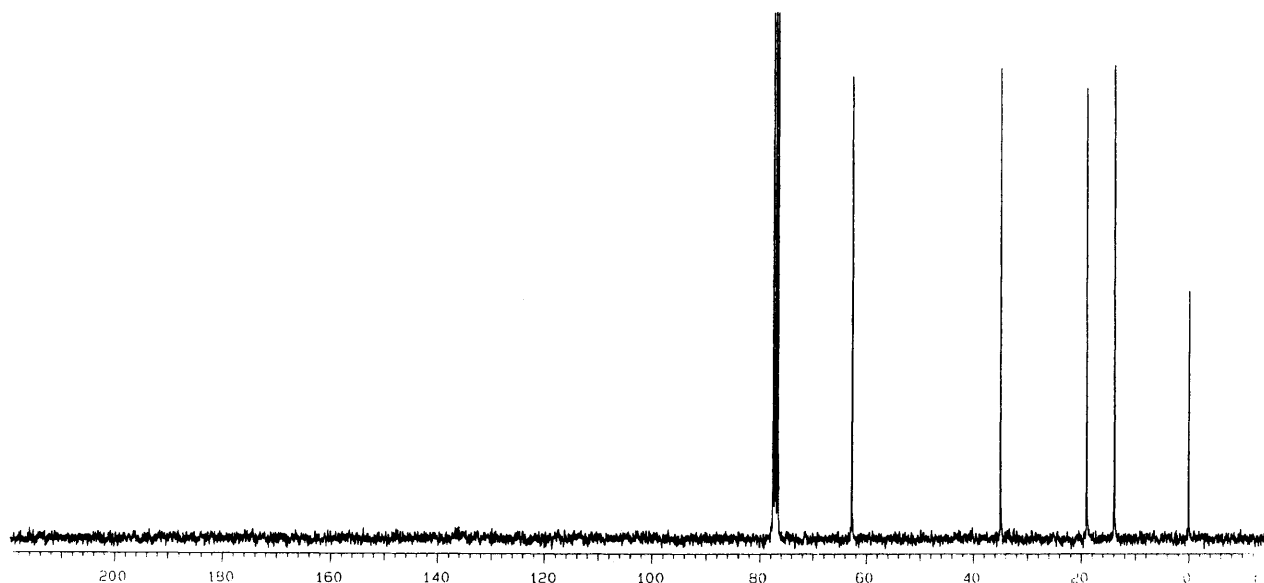
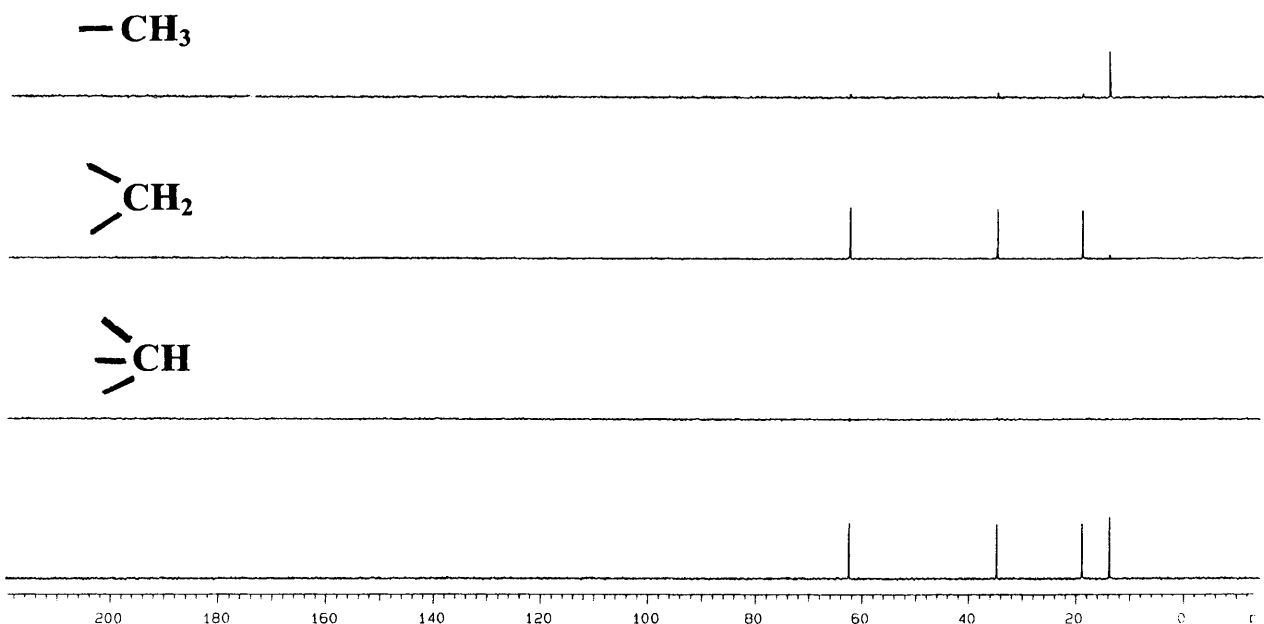
If the carbon atom does not have any attached hydrogen atoms, it remains a singlet. If it has one attached hydrogen atom, it is split into a doublet. If it has two attached hydrogen atoms, then two equal splittings give a triplet with peaks in the ratio 1 : 2 : 1. Since having  $n$  attached hydrogens splits the peak into  $(n + 1)$  peaks, this is known as the  $(n + 1)$  rule (Diagram 5.1). We can now tell how many different carbon atoms the molecule has, and how many hydrogen atoms are attached to each carbon atom.

This method works well in a molecule which has well spaced  $^{13}\text{C}$  peaks, but is less successful in larger molecules. An alternative method is to measure what is known as a DEPT spectrum (Distortionless Enhancement by Polarisation Transfer). The DEPT spectrum plots the  $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$  peaks separately. It does not record carbon atoms which do not have a hydrogen atom attached, so we need a decoupled spectrum as well as a DEPT spectrum. The spectra for butan-1-ol are shown in Figure 5.2.

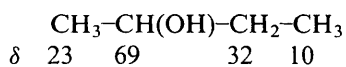
The  $^{13}\text{C}$  NMR spectrum of butan-1-ol thus consists of four peaks (+  $\text{CDCl}_3$  and TMS),  $\underline{\text{C}}\text{H}_3$  at  $\delta 14$ , and  $\underline{\text{C}}\text{H}_2$  at  $\delta 19$ , 35 and 63. Their  $\delta$  values depend on the distance from the electronegative oxygen atom. Furthest downfield at  $\delta 63$  is the  $\text{CH}_2$  group attached to the OH group. The influence of this oxygen is strong, and also affects the next  $\text{CH}_2$  at  $\delta 35$ , but the next  $\text{CH}_2$  at  $\delta 19$  is almost unaffected. The  $\text{CH}_3$  is at  $\delta 14$ .

Almost all  $^{13}\text{C}$  NMR peaks are found downfield from TMS, extending to about 200 $\delta$ . Exact chemical shifts depend on the group itself, and on neighbouring electronegative groups. Thus, alkyl substitution of a  $\text{CH}_3$  group, making it a  $\text{CH}_2$  group, moves the absorption at  $\delta 8.4$  down to  $\delta 15.9$ ; a second substitution makes it a  $\text{CH}$  group at  $\delta 25.0$ . The most useful chemical shifts are listed in Table 5.1. It is also useful to have the ranges of chemical shifts of the substituted alkyl groups, and these are given in Table 5.2.



**DECOUPLED SPECTRUM****DEPT SPECTRUM****Figure 5.2**

The next spectrum, shown in Figure 5.3, is that of butan-2-ol,  $\text{CH}_3\text{--CH(OH)--CH}_2\text{--CH}_3$ . Again, the decoupled spectrum consists of four peaks, so all carbon atoms are different. The DEPT spectrum shows that we have a  $\text{CH}$  at  $\delta 69$ , a  $\text{CH}_2$  at  $\delta 32$  and two  $\text{CH}_3$  groups at  $\delta 23$  and  $10$ . The peak at  $\delta 69$  is clearly that of the carbon atom attached to the oxygen, on the grounds of both chemical shift and splitting. The  $\text{CH}_3$  group at  $\delta 23$ , being downfield of the other  $\text{CH}_3$ , must be the one attached to the  $\text{CH(OH)}$ . The molecule is thus



**Table 5.1**  $^{13}\text{C}$  NMR chemical shifts

Group	$^{13}\text{C}$ chemical shift $\delta$ (ppm)	
	Attached to groups of low electronegativity	Full range
$\text{CH}_3$	8	5–70
$\text{CH}_2$	16	10–80
$\text{CH}$	25	20–90
$\text{C}=\text{C}$	67	65–80
$\text{C}\equiv\text{N}$	118	115–130
$\text{C}=\text{C}$	123	100–170
Ph	128	110–170
$\text{C}=\text{O}$ ester	170	160–180
$\text{C}=\text{O}$ acid	178	170–190
$\text{C}=\text{O}$ ketone or aldehyde	200	190–210

**Table 5.2** Effect of electronegative groups on  $^{13}\text{C}$  chemical shifts

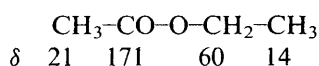
Group	Chemical shift $\delta$ (ppm) when next to				
	Alkyl	$\text{C}=\text{O}$	$\text{C}=\text{C}$	Ph	$-\text{OR}^*$
$\text{CH}_3$	8–30	20–35	20–30	20–45	55–70
$\text{CH}_2$	15–40	25–40	20–40	35–55	50–80
$\text{CH}$	20–50	30–40	25–40	40–60	65–90

\*R = H or alkyl.

The peaks from the carbon atoms of an aromatic ring show a strong downfield shift, as shown in Table 5.1. In the case of the  $^{13}\text{C}$  NMR spectrum of methylbenzene (toluene),  $\text{PhCH}_3$ , shown in Figure 5.4, the aromatic carbon peaks are in the range of  $\delta 120$ – $140$ . Furthest downfield is the carbon attached to the methyl group. The other carbon atoms are moved downfield by amounts depending on their position relative to the methyl group. The methyl group itself is at  $\delta 21$ , moved downfield by the phenyl ring.

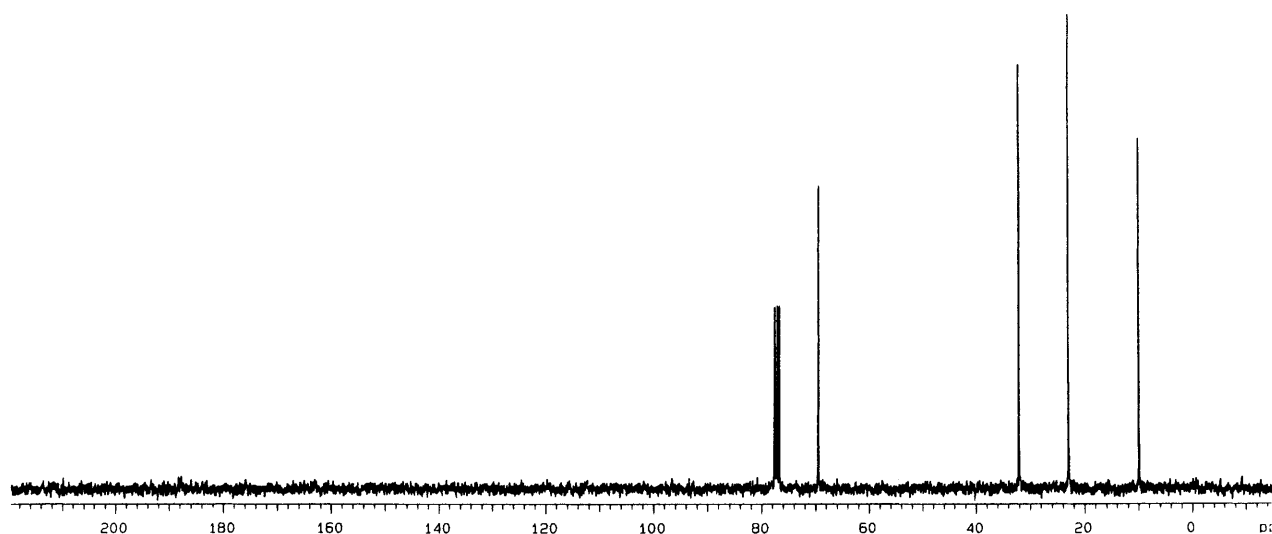
We can now tackle a few spectra of unknown molecules. The first is shown in Figure 5.5. The substance has the molecular formula  $\text{C}_4\text{H}_8\text{O}_2$ , and has  $^{13}\text{C}$  NMR peaks at  $\delta 171$ , 60, 21 and 14. Thus, all four carbon atoms show separately on the decoupled spectrum. The peak at  $\delta 171$  does not show in the DEPT spectrum, so is a quaternary carbon atom. The peak at  $\delta 60$  is a  $\text{CH}_2$  carbon atom, while the peaks at  $\delta 21$  and 14 are  $\text{CH}_3$  groups. We thus have a  $\text{CH}_2$  and two  $\text{CH}_3$  groups, accounting for all eight hydrogen atoms. We also have only two ‘chain ending’ groups (groups which can bond to only one other group; in this case, the two  $\text{CH}_3$  groups) so the molecule cannot have a branched chain.

We can account for  $\text{C}_4\text{H}_8$  from the spectrum, out of  $\text{C}_4\text{H}_8\text{O}_2$ , so have to consider two oxygen atoms. The chemical shift of the quaternary carbon atom is  $\delta 171$ , suggesting it is part of an ester linkage. The chemical shift of the  $\text{CH}_2$  at  $\delta 60$  suggests it is attached to the ester oxygen. The more downfield of the  $\text{CH}_3$  groups is attached to the carbonyl oxygen. The molecule is thus ethyl acetate:



The next unknown has the spectrum shown in Figure 5.6. The molecule is  $\text{C}_5\text{H}_8\text{O}$ , and it has  $^{13}\text{C}$  NMR peaks at  $\delta 220$ , 38 and 23. In this case, the

## DECOUPLED SPECTRUM



## DEPT SPECTRUM

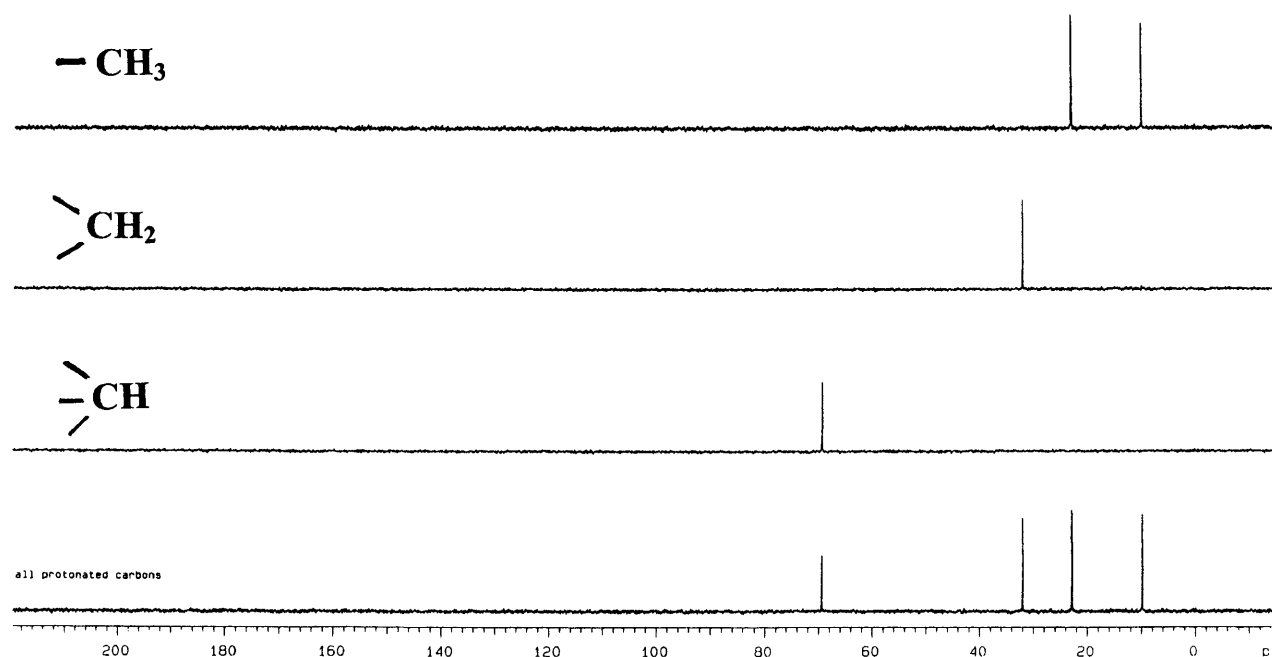
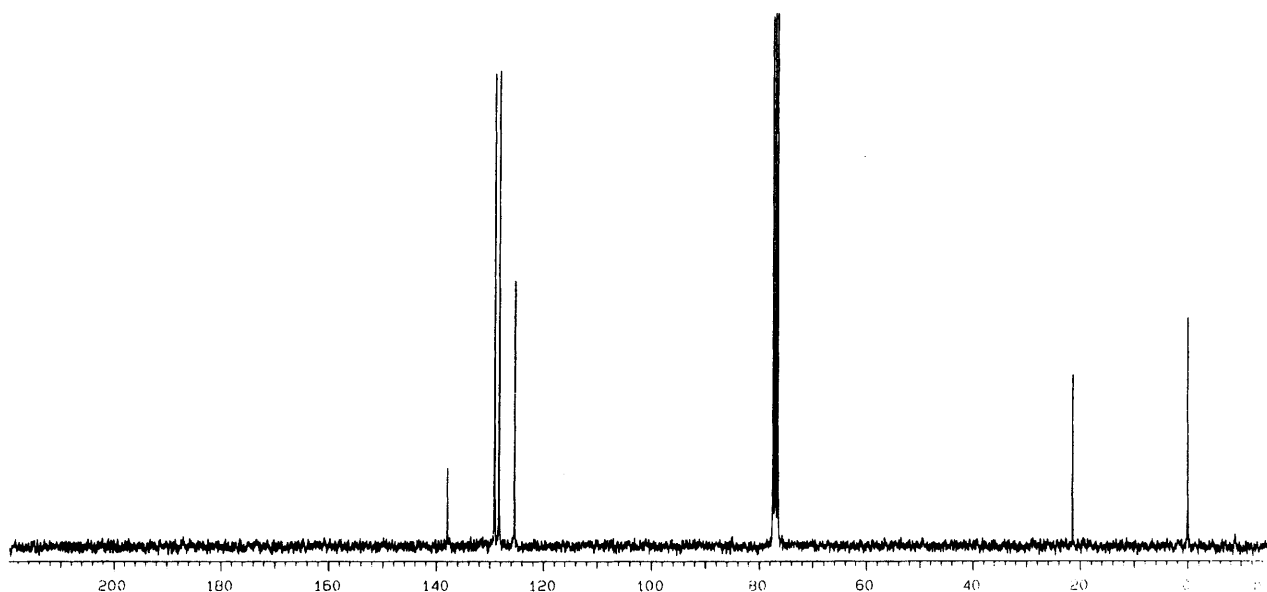


Figure 5.3

molecule has enough symmetry to put two pairs of atoms in identical environments. The peak at  $\delta 220$  does not show in the DEPT spectrum, so is a quaternary carbon atom. The peaks at  $\delta 38$  and  $23$  are both  $\text{CH}_2$  groups, which accounts for only four out of eight hydrogen atoms. The molecule must thus consist of a quaternary carbon atom, two pairs of identical  $\text{CH}_2$  groups, and one remaining oxygen. It is noticeable that the molecule does not have any chain ending groups, so it must be cyclic.

On the basis of its chemical shift, the quaternary carbon at  $\delta 220$  is probably part of a ketone carbonyl group, which accounts for the oxygen atom. Chemical shifts also indicate that the carbon atoms with  $\delta 38$  are closer to the

## DECOUPLED SPECTRUM



## DEPT SPECTRUM

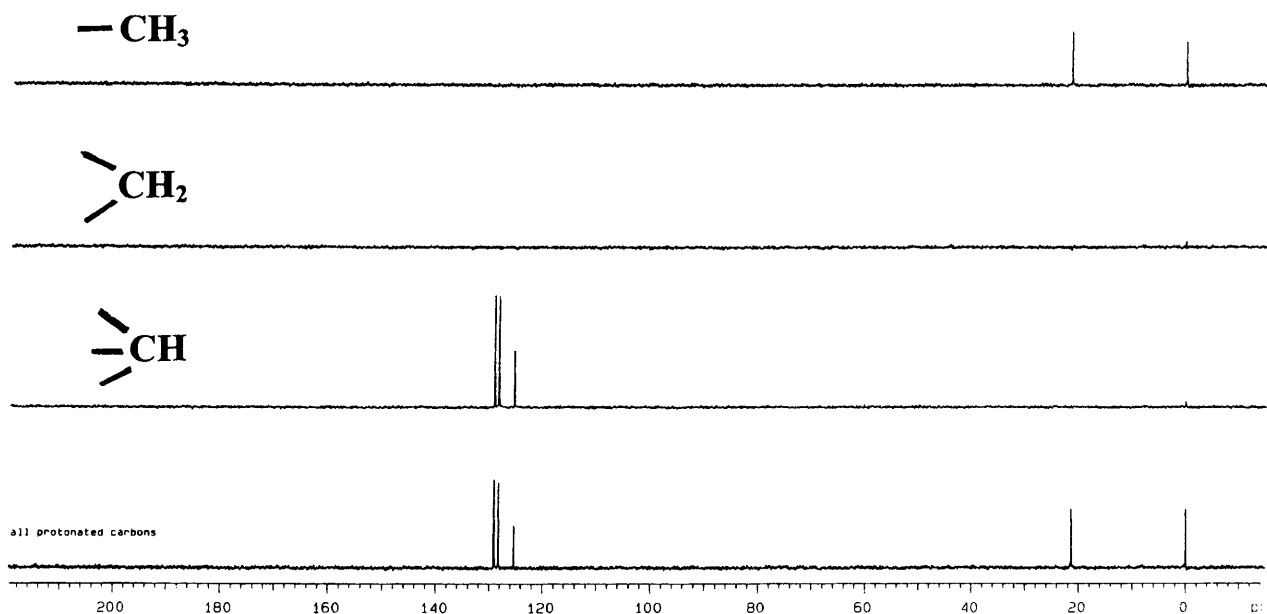
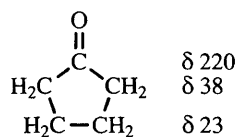


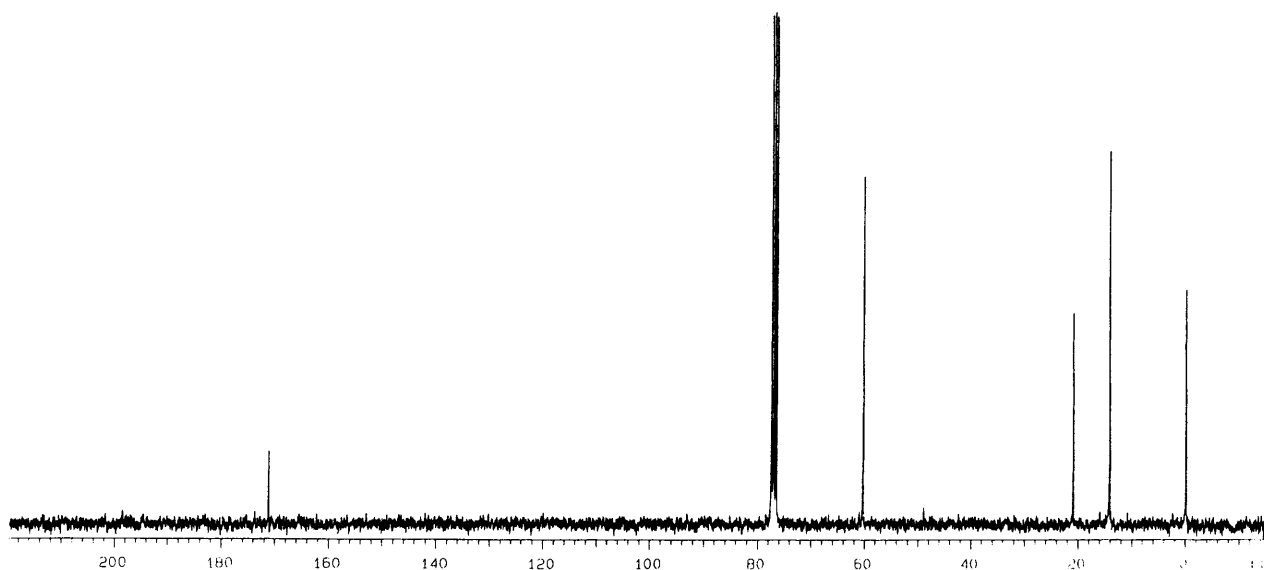
Figure 5.4

carbonyl group than those with  $\delta 23$ . The molecule is thus cyclopentanone:



The next unknown, whose spectrum is shown in Figure 5.7, has a molecular formula  $\text{C}_6\text{H}_{12}$ . The  $^{13}\text{C}$  NMR spectrum has peaks at  $\delta 139$  (CH), 114 ( $\text{CH}_2$ ), 34 ( $\text{CH}_2$ ), 31 ( $\text{CH}_2$ ), 22 ( $\text{CH}_2$ ) and 14 ( $\text{CH}_3$ ). We can thus account for all six carbon atoms, all in different environments, and all 12 hydrogen atoms. On

## DECOUPLED SPECTRUM



## DEPT SPECTRUM

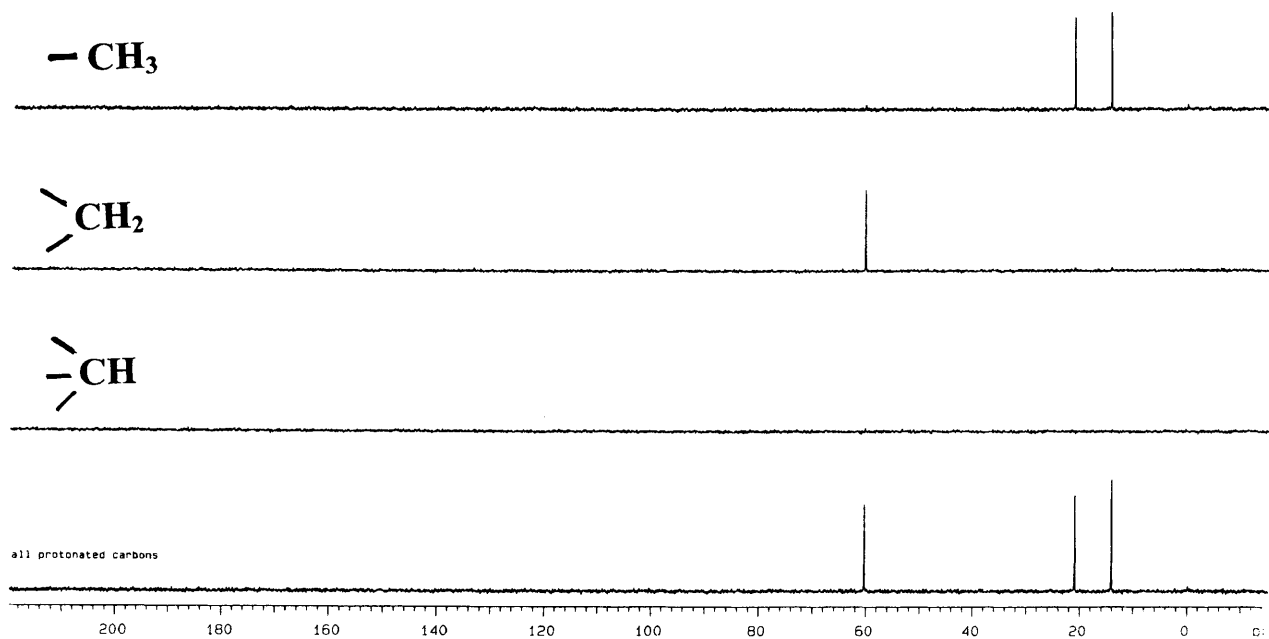
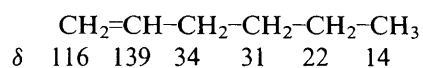


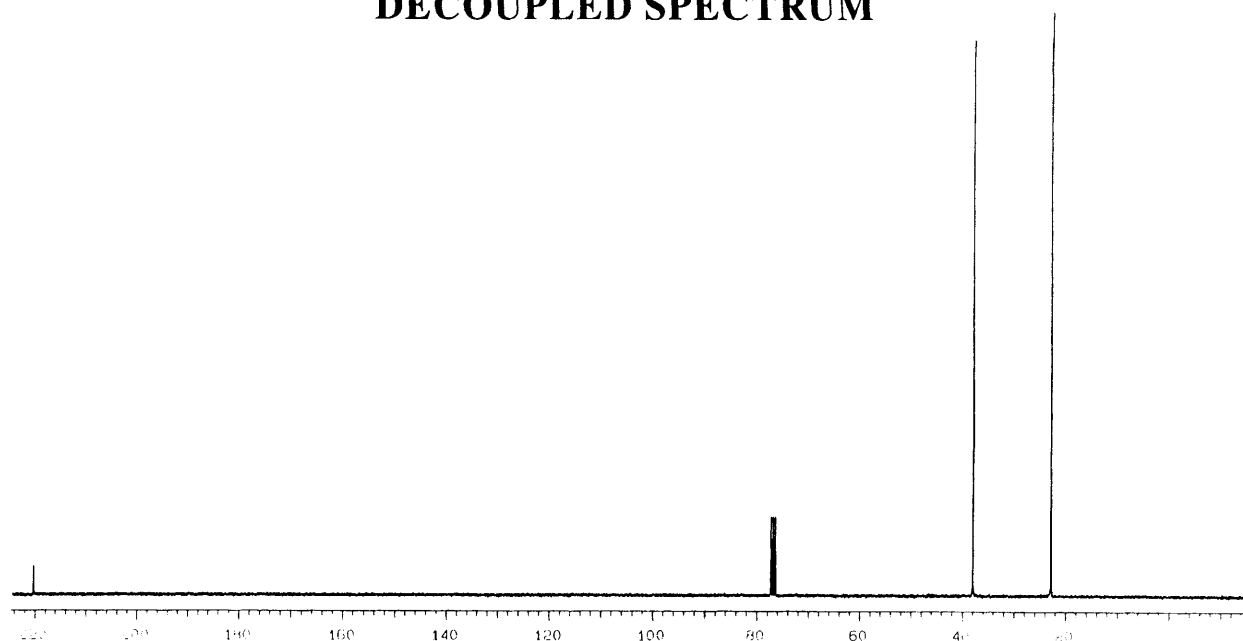
Figure 5.5

the basis of chemical shift, the carbon atoms at  $\delta$ 139 and 114 are probably atoms of a carbon double bond; since the latter is a  $\text{CH}_2$  group, then the group is  $-\text{CH}=\text{CH}_2$ . This group and the methyl group provide the only chain ending groups, so the molecule must be a straight chain hydrocarbon, hex-1-ene:



It is easy to assign a straight chain structure like this, but if we had an extra methyl group on C-3 or C-4 it would be difficult to be sure which carbon atom

## DECOUPLED SPECTRUM



## DEPT SPECTRUM

$-\text{CH}_3$



$\text{>CH}_2$



$\text{>CH}$

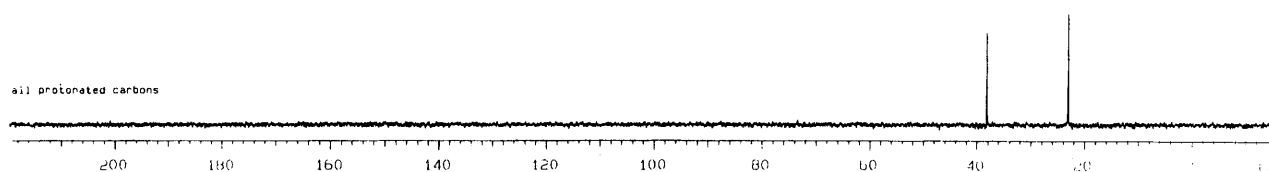
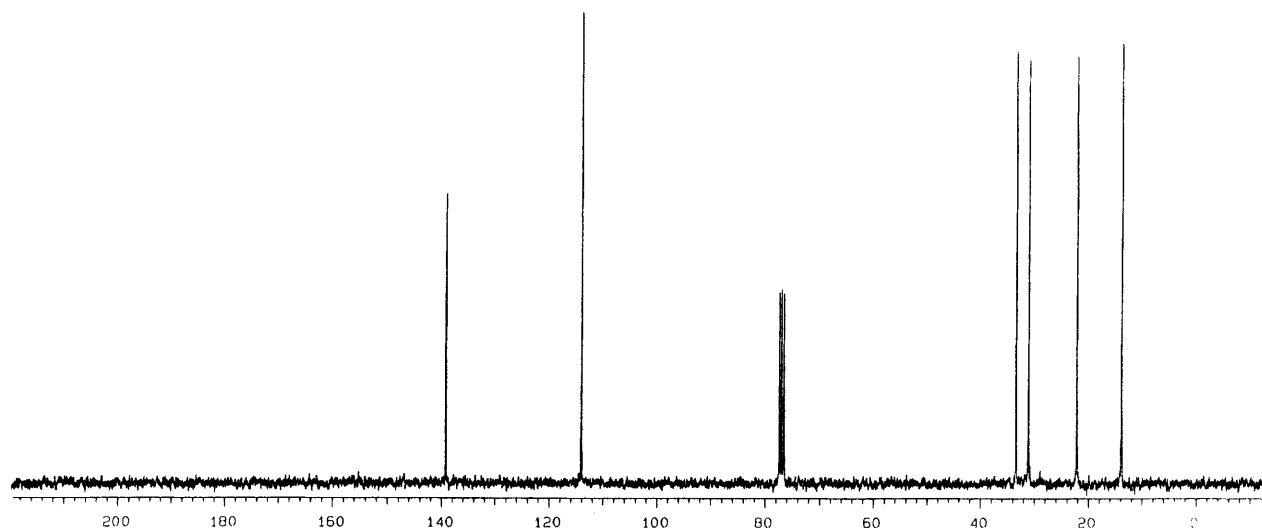


Figure 5.6

it was attached to. A methyl group on C-5 would be identical to C-6, and easy to assign. It is a general difficulty of  $^{13}\text{C}$  assignment that branched chains can be difficult to assign unless symmetry considerations help.

The next unknown, shown in Figure 5.8, has the molecular formula  $\text{C}_8\text{H}_{16}$ . The spectrum has peaks at  $\delta 130$  ( $\text{CH}$ ), 35 ( $\text{CH}_2$ ), 23 ( $\text{CH}_2$ ) and 14 ( $\text{CH}_3$ ). This accounts for only  $\text{C}_4\text{H}_8$ , suggesting that the molecule has a plane of symmetry, with two  $\text{C}_4\text{H}_8$  units, one each side of the plane. The chemical shift of the peak at  $\delta 130$  suggests that it is part of a double bond. Since it is only half of a double bond, the plane of symmetry must bisect the double

## DECOUPLED SPECTRUM



## DEPT SPECTRUM

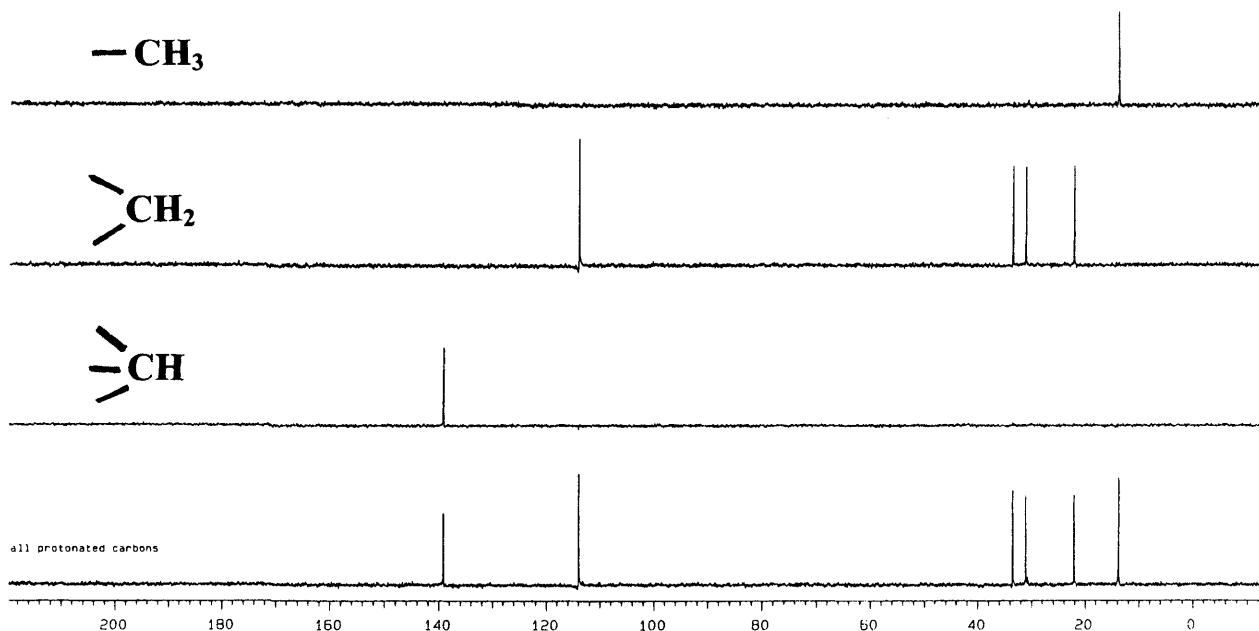
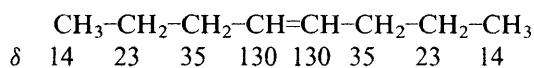


Figure 5.7

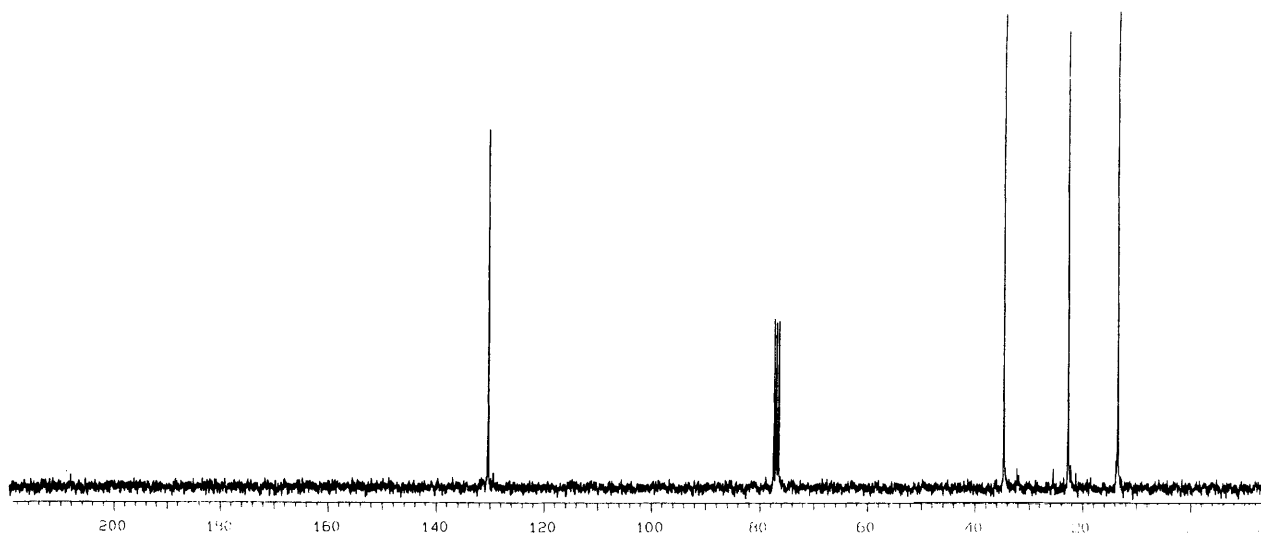
bond. The whole molecule has only two chain ending groups, so is linear. It is clearly oct-4-ene:



We cannot, on the basis of this single spectrum, say whether the double bond is *cis* or *trans* (*E* or *Z*) (it is actually *trans*). In some cases, we could not distinguish the isomers even if we had spectra of authentic samples available. This is a restriction of <sup>13</sup>C NMR, though the problem can often be solved by <sup>1</sup>H NMR.

Our final example has the spectrum shown in Figure 5.9, and has the molecular formula C<sub>5</sub>H<sub>10</sub>O. It has peaks at  $\delta$  136 (C), 124 (CH), 59 (CH<sub>2</sub>), 26

## DECOUPLED SPECTRUM



## DEPT SPECTRUM

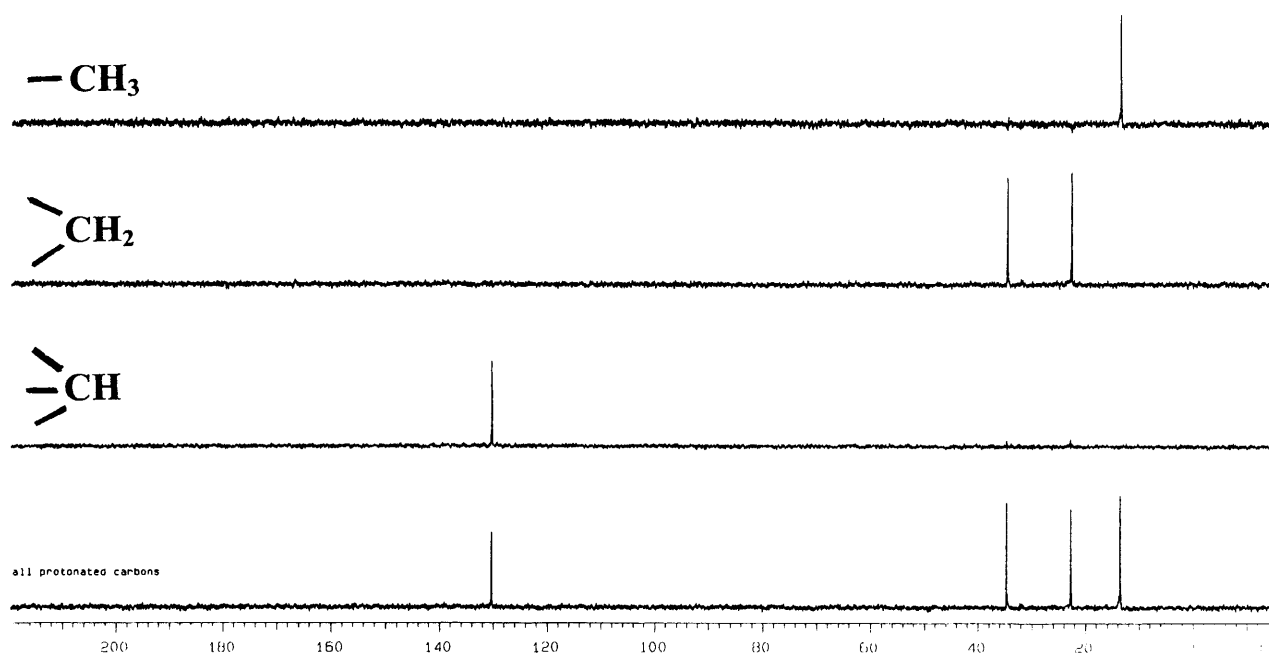
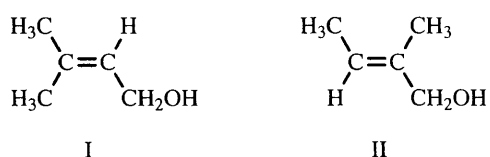


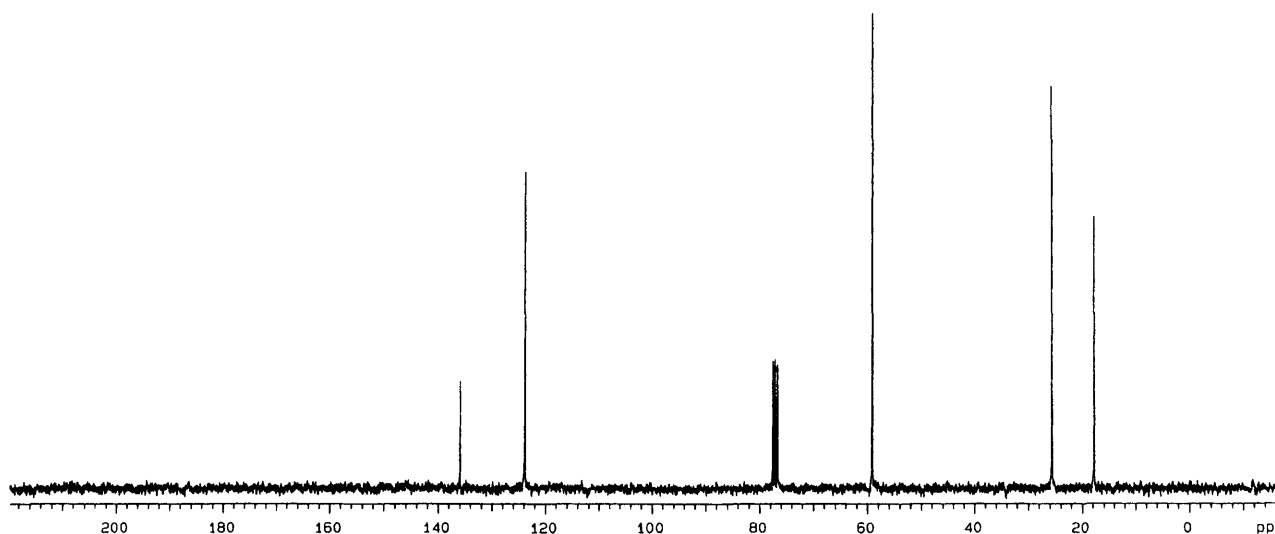
Figure 5.8

(CH<sub>3</sub>) and 18 (CH<sub>3</sub>). This accounts for five carbon atoms and nine hydrogen atoms, leaving OH, which suggest the molecule is an alcohol. Chemical shifts show the peaks at  $\delta$ 136 and 124 to be part of a double bond, HC=C, and the peak at  $\delta$ 59 is a CH<sub>2</sub> which must be attached to the OH group. The molecule has three chain ending groups, CH<sub>3</sub>, CH<sub>3</sub> and CH<sub>2</sub>OH, so it cannot be linear; these three groups must be attached to the double bond. We can do this in two ways:





## DECOUPLED SPECTRUM



## DEPT SPECTRUM

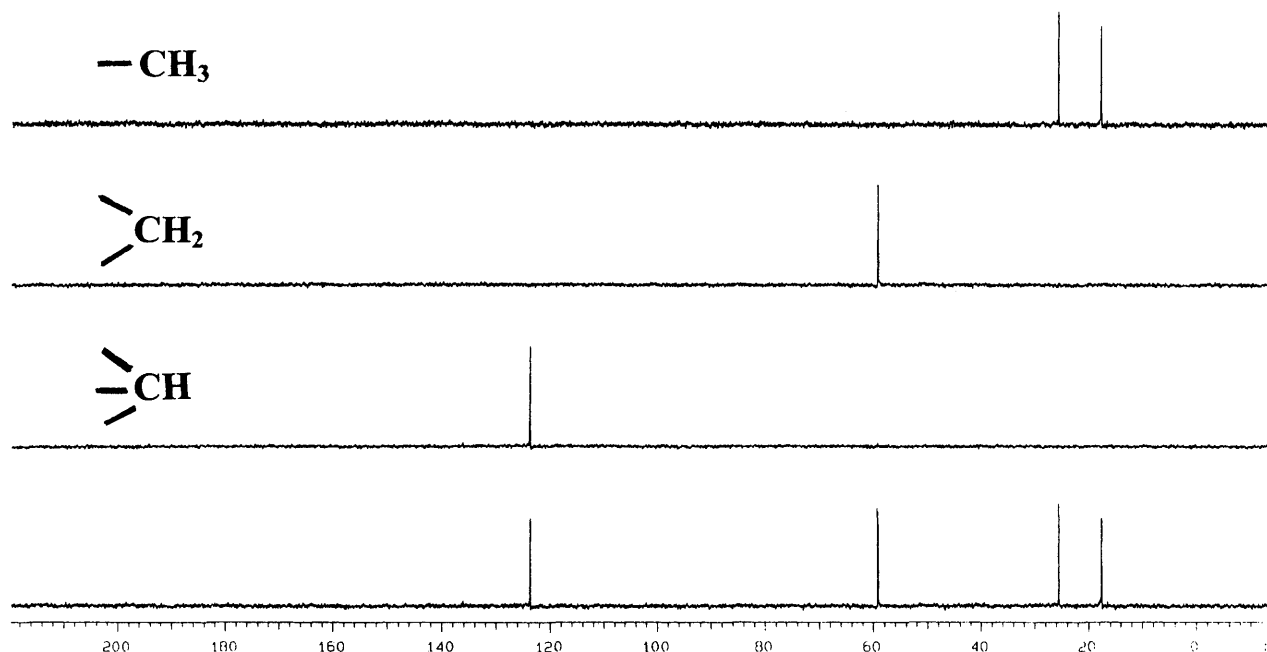


Figure 5.9

We cannot distinguish between these possible structures on the basis of the spectrum in Figure 5.9. Having spectra of I and II should allow us to make the distinction (Figure 5.9 is actually the spectrum of 3-methylbut-2-en-1-ol, I). This highlights the main problem of interpreting <sup>13</sup>C NMR spectra: we cannot always tell which carbon atom is next to which. In simple molecules, it may not matter, or the effect of a strong electronegative group may help. Symmetry is also useful, but many large molecules have <sup>13</sup>C spectra which cannot be easily assigned. The problem can be solved by <sup>1</sup>H NMR.

### Summary

When we have a  $^{13}\text{C}$  NMR spectrum to assign, the following steps are a useful approach:

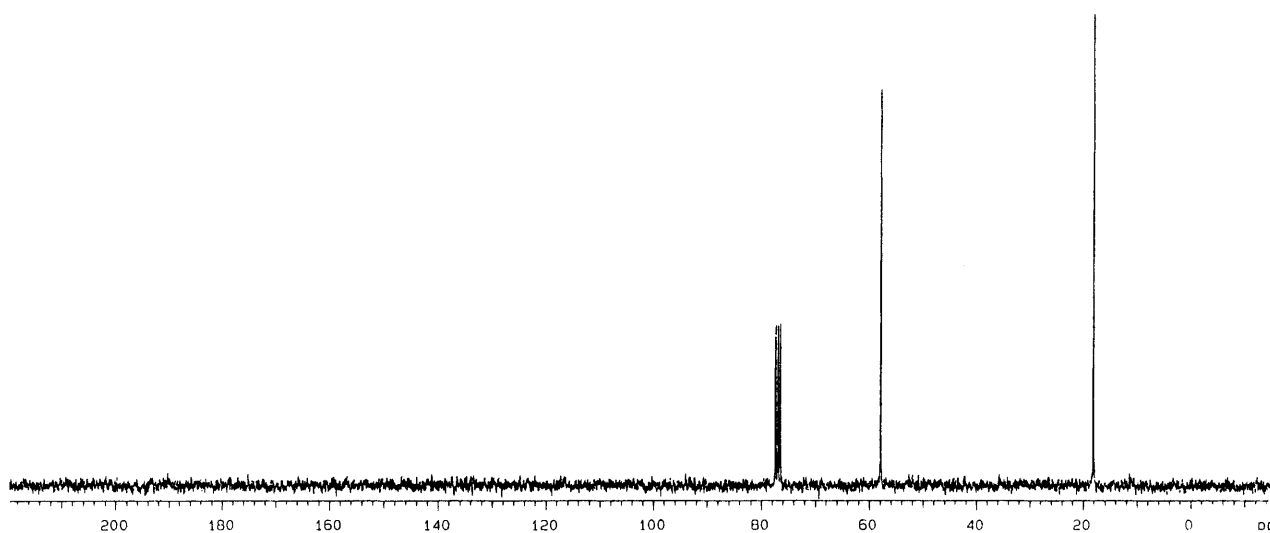
- A. Count the number of peaks in the decoupled spectrum. Compare the figure with the molecular formula. If you have more carbon atoms than peaks, then at least one peak represents more than one carbon atom.
- B. Calculate the total number of hydrogen atoms on the carbon atoms, and see if this fits with the number of hydrogen atoms in the molecule. When you have allowed for identical groups, any hydrogen left must be attached to an element other than carbon.
- C. See if any of the carbon atoms shown in the spectrum are part of recognisable groups, such as carbonyl groups, aromatic rings, double bonds, nitrile groups, *etc.*
- D. See how many chain ending groups (*i.e.* groups with only one attachment to other atoms remaining) the molecule has. Zero implies a ring, one a substituted ring, two a straight chain or disubstituted ring and more than two a branched chain or polysubstituted ring.
- E. Look at the molecular formula for atoms such as O, N, S, halogen. They can give useful clues as to the cause of large downfield shifts.
- F. Relate chemical shifts to electronegative groups in the molecule.

In complex spectra, it is often possible to suggest several structures consistent with a  $^{13}\text{C}$  NMR spectrum. Some of these may be eliminated on the grounds of symmetry, but in some cases a precise identification is not possible. The  $^1\text{H}$  NMR spectrum will help in many cases, but cyclic systems have very complex  $^1\text{H}$  NMR spectra and are more easily identified from  $^{13}\text{C}$  spectra.

### Problems in Interpreting $^{13}\text{C}$ NMR Spectra

You are given the decoupled and DEPT spectra of 10 samples, together with the molecular formula. In all cases, you should be able to identify the structure of the sample from the data provided.

# DECOUPLED SPECTRUM C<sub>2</sub>H<sub>6</sub>O



## DEPT SPECTRUM

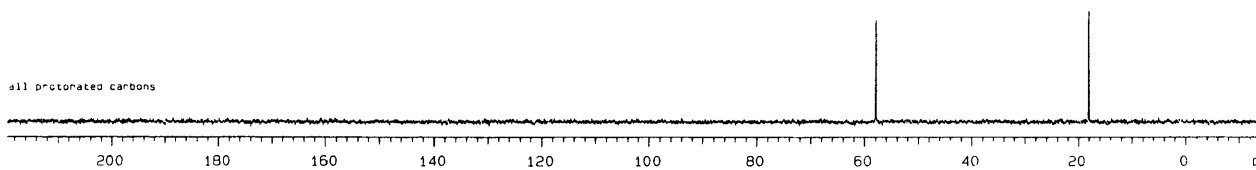
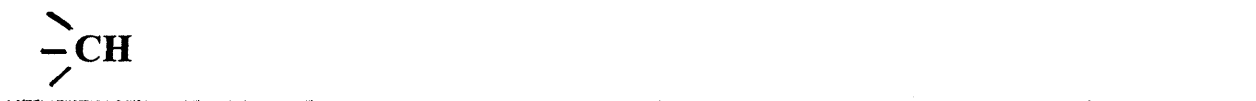
—CH<sub>3</sub>



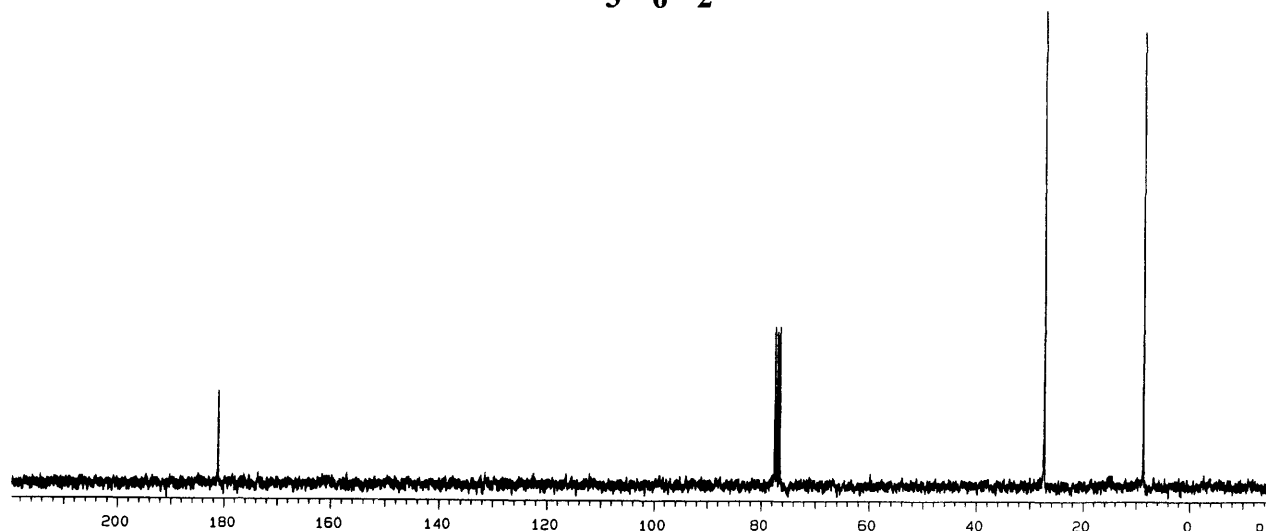
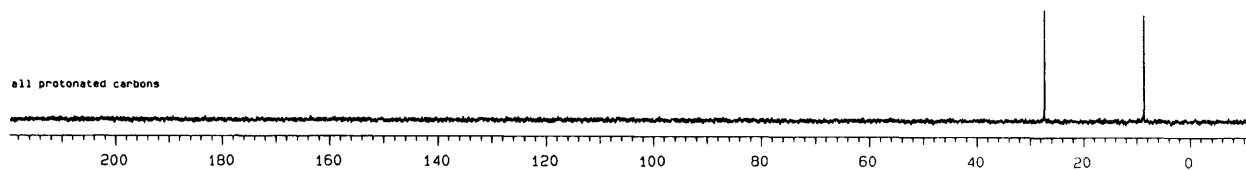
>CH<sub>2</sub>



>CH

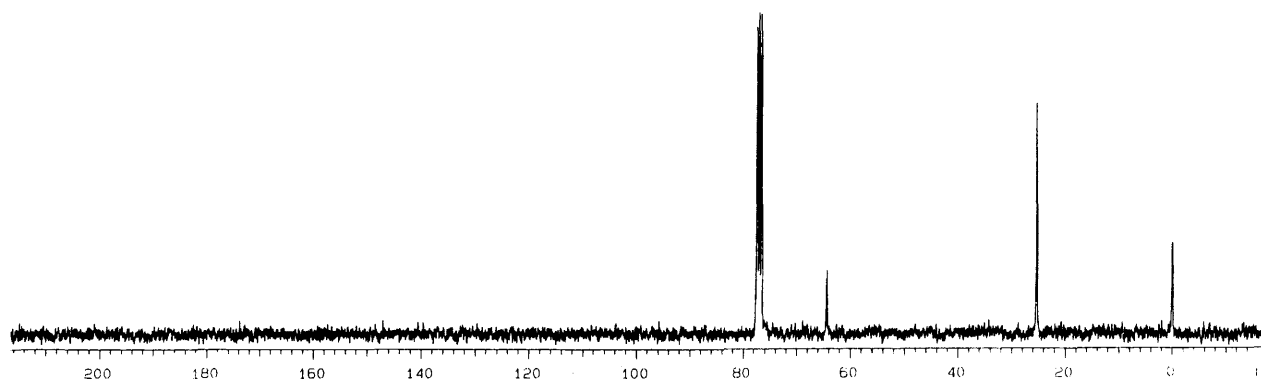


Sample 5.1

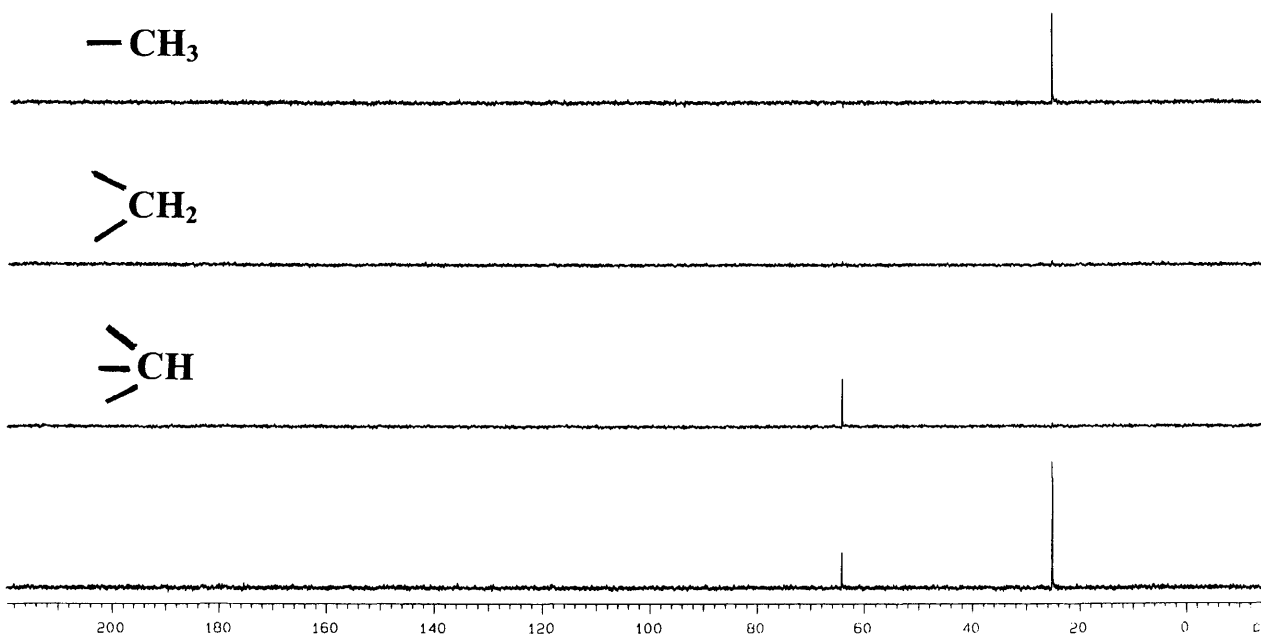
**DECOUPLED SPECTRUM****DEPT SPECTRUM** $-\text{CH}_3$  $-\text{CH}_2-$  $-\text{CH}-$ 

Sample 5.2

# DECOUPLED SPECTRUM C<sub>3</sub>H<sub>8</sub>O



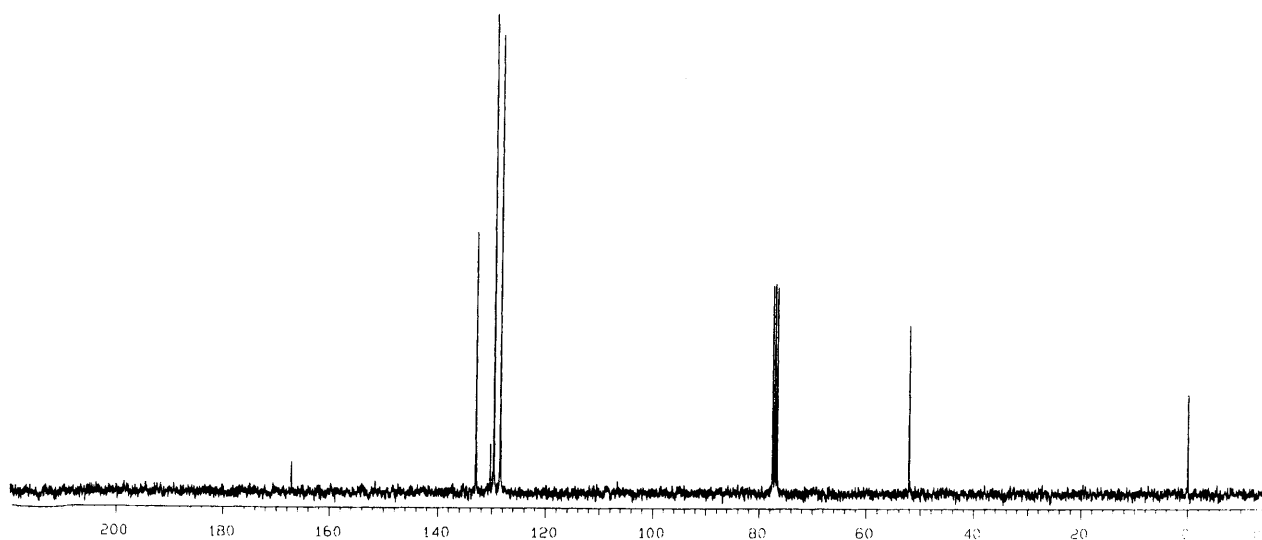
## DEPT SPECTRUM



Sample 5.3

# DECOUPLED SPECTRUM

$C_8H_8O_2$



## DEPT SPECTRUM

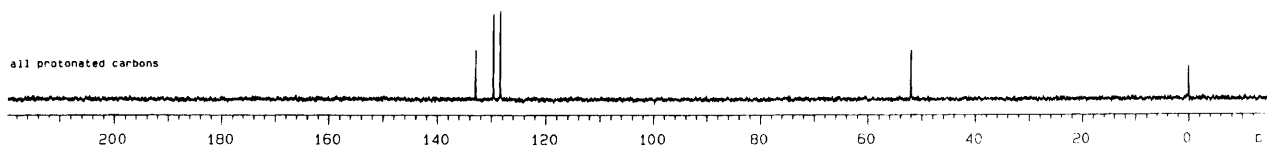
$-CH_3$



$\text{>CH}_2$

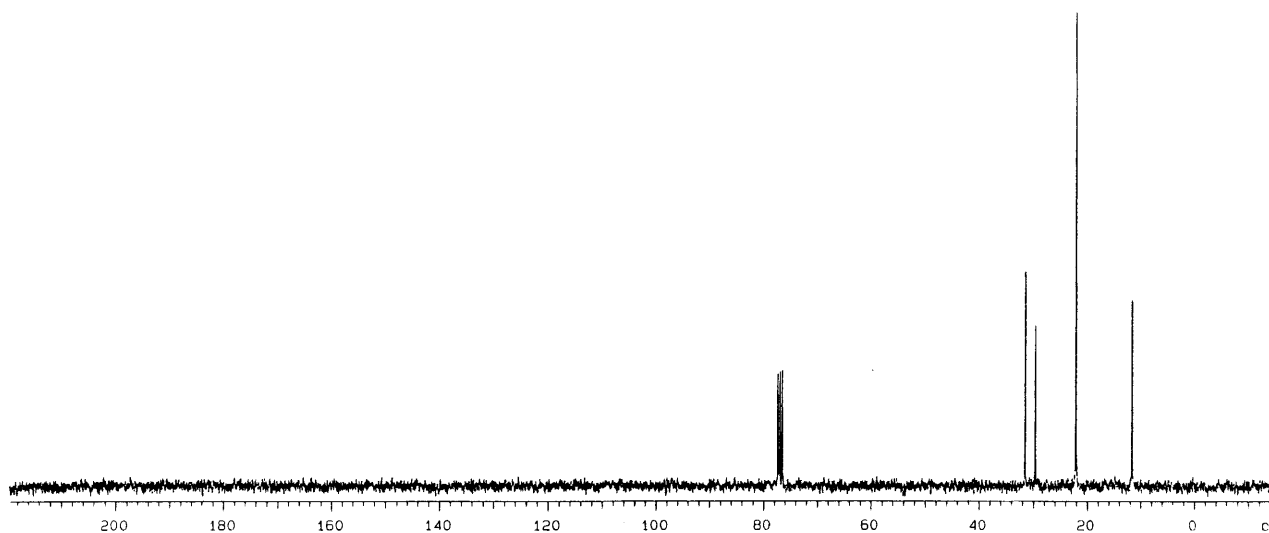


$\text{=CH}$

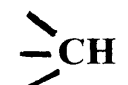
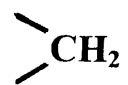


Sample 5.4

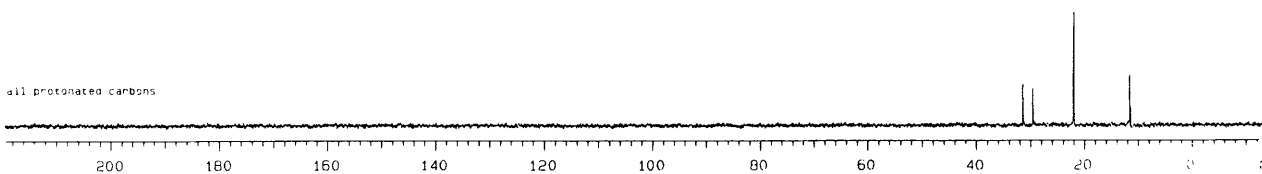
## DECOUPLED SPECTRUM



## DEPT SPECTRUM



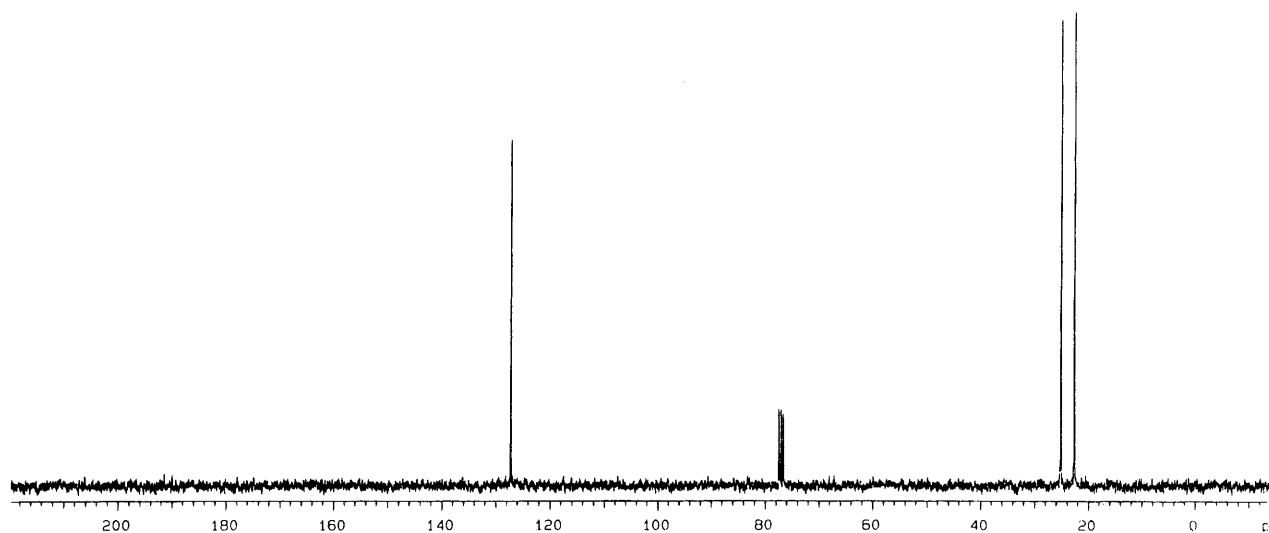
all protonated carbons



Sample 5.5

# DECOUPLED SPECTRUM

$C_6H_{10}$

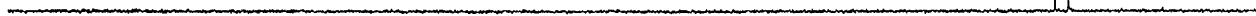


## DEPT SPECTRUM

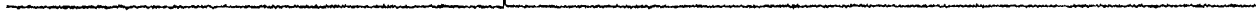
$-CH_3$



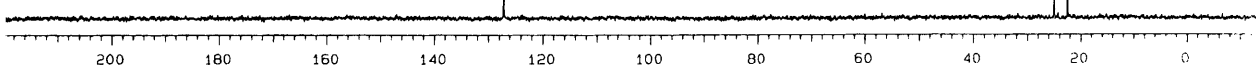
$\backslash CH_2$



$\backslash CH$



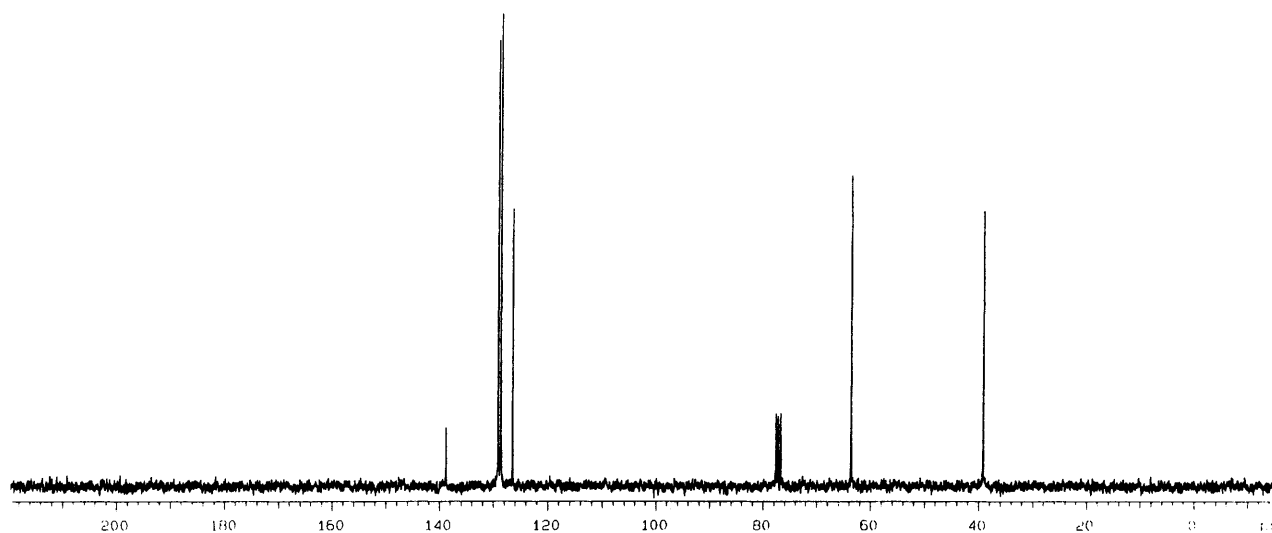
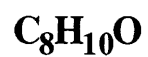
all protonated carbons



Sample 5.6



## DECOUPLED SPECTRUM

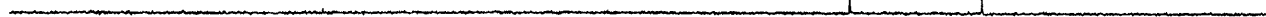


## DEPT SPECTRUM

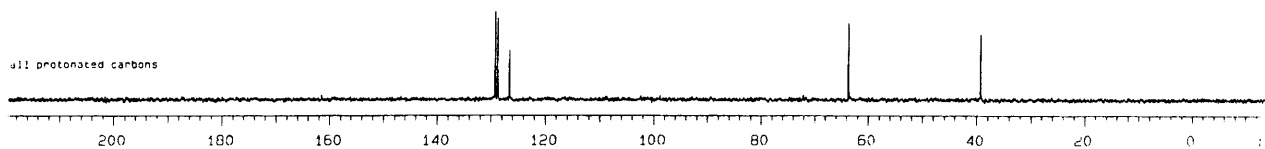
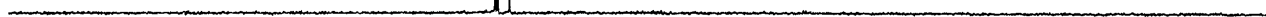
$\text{—CH}_3$



$\text{>CH}_2$



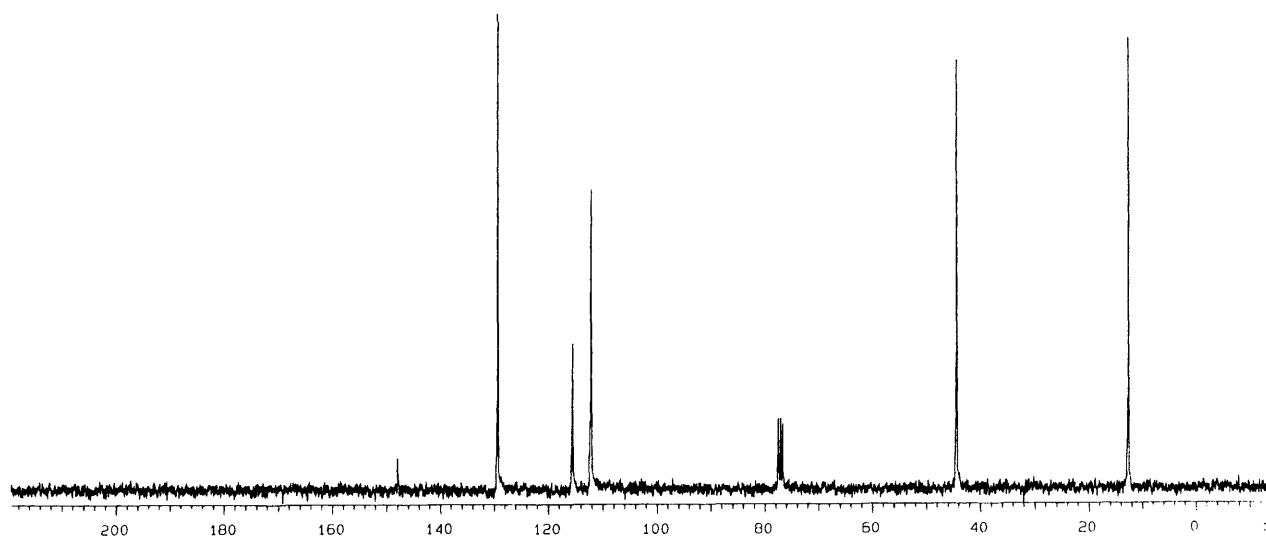
$\text{=CH}$



Sample 5.7

# DECOUPLED SPECTRUM

$\text{C}_{10}\text{H}_{15}\text{N}$



## DEPT SPECTRUM

$-\text{CH}_3$



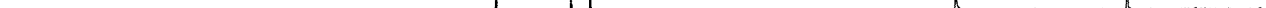
$\text{>CH}_2$



$\text{>CH}$



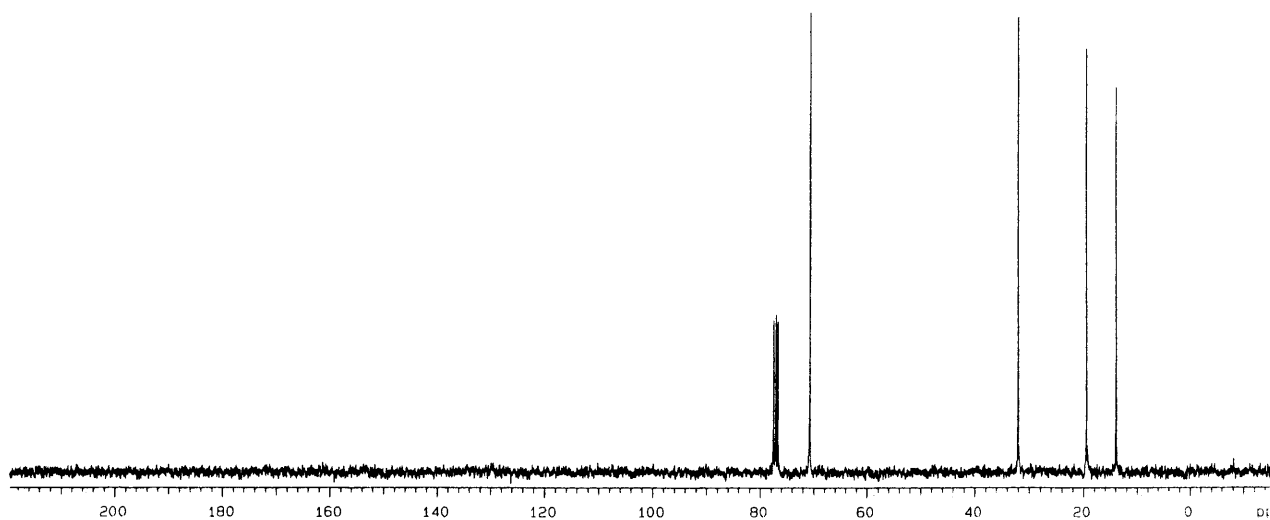
all protonated carbons



Sample 5.8

# DECOUPLED SPECTRUM

**C<sub>8</sub>H<sub>18</sub>O**



## DEPT SPECTRUM

**—CH<sub>3</sub>**



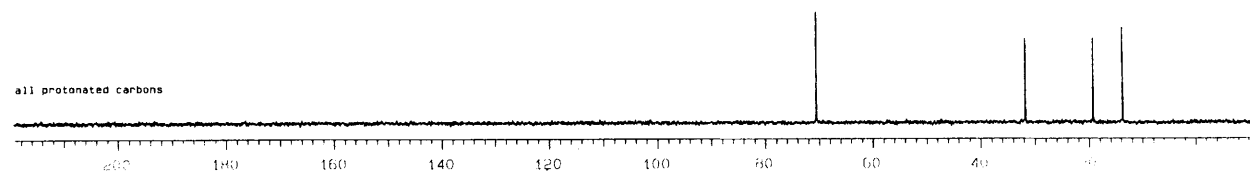
**>CH<sub>2</sub>**



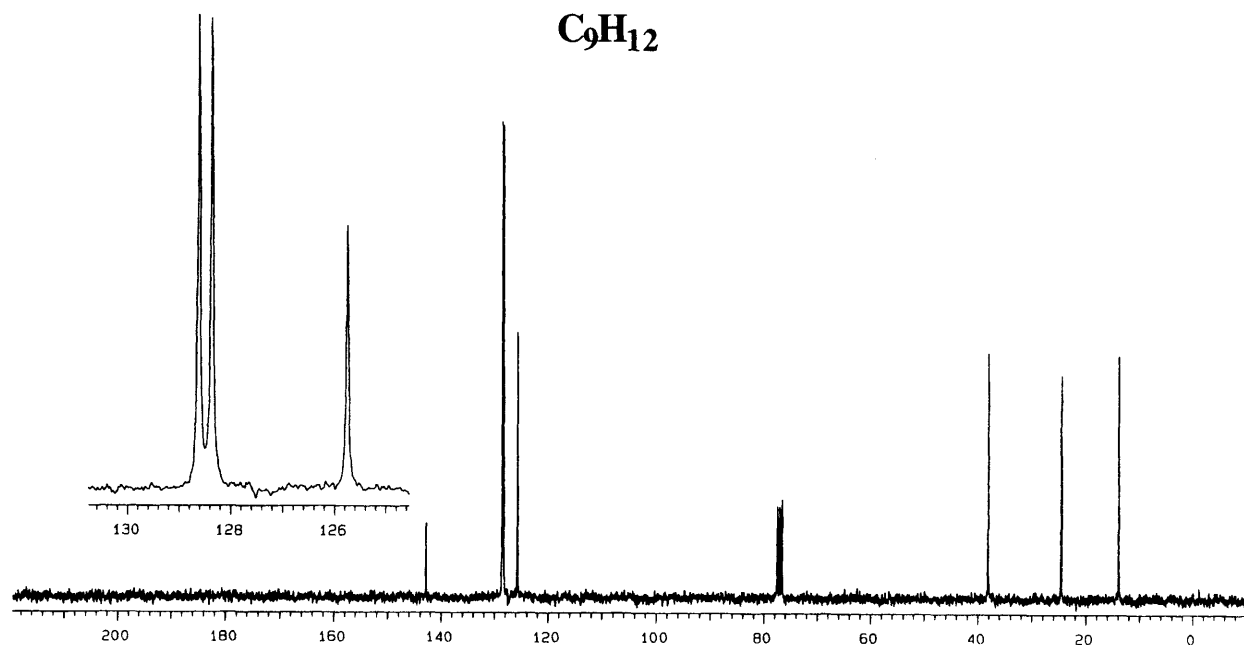
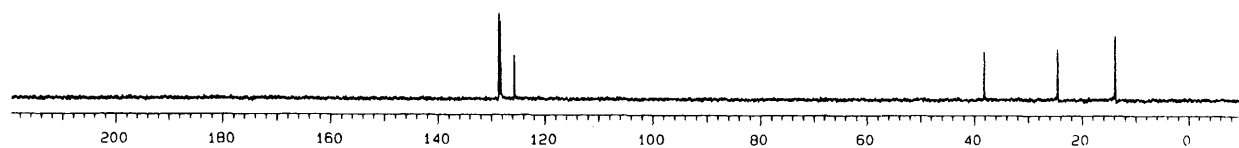
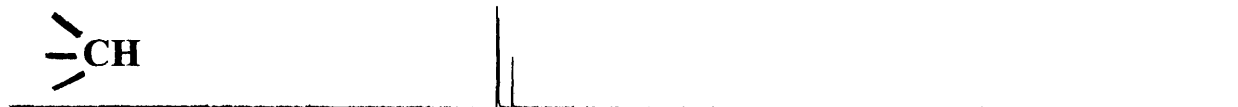
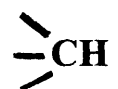
**>CH**



all protonated carbons



Sample 5.9

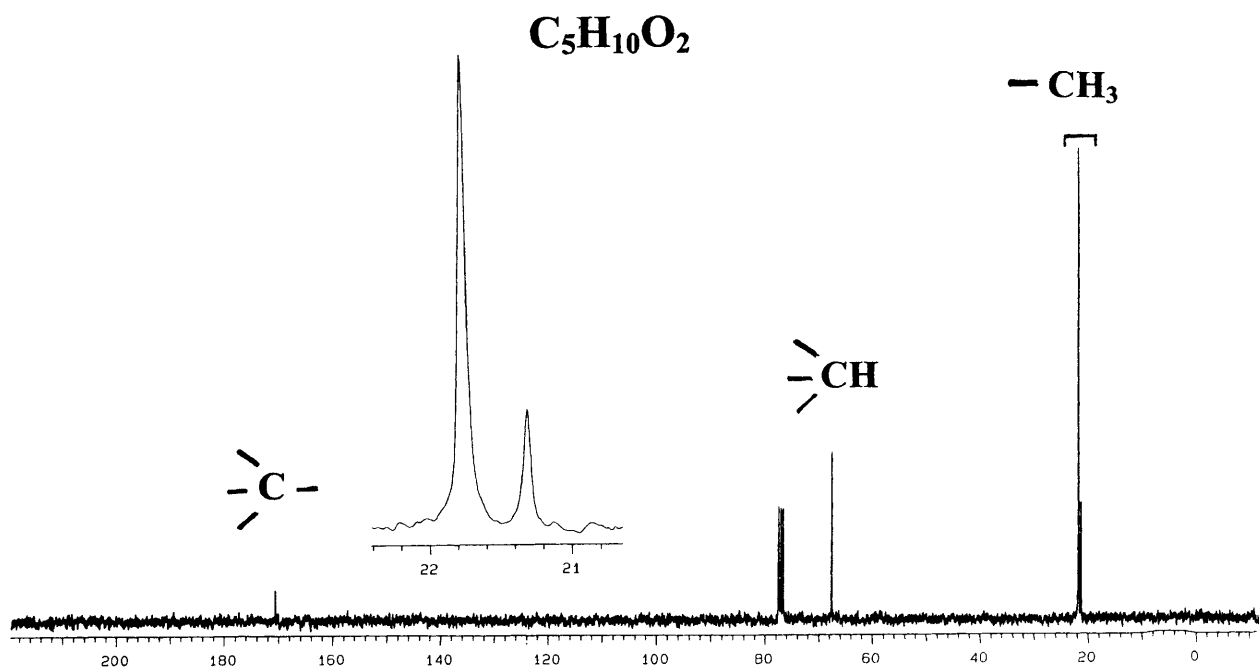
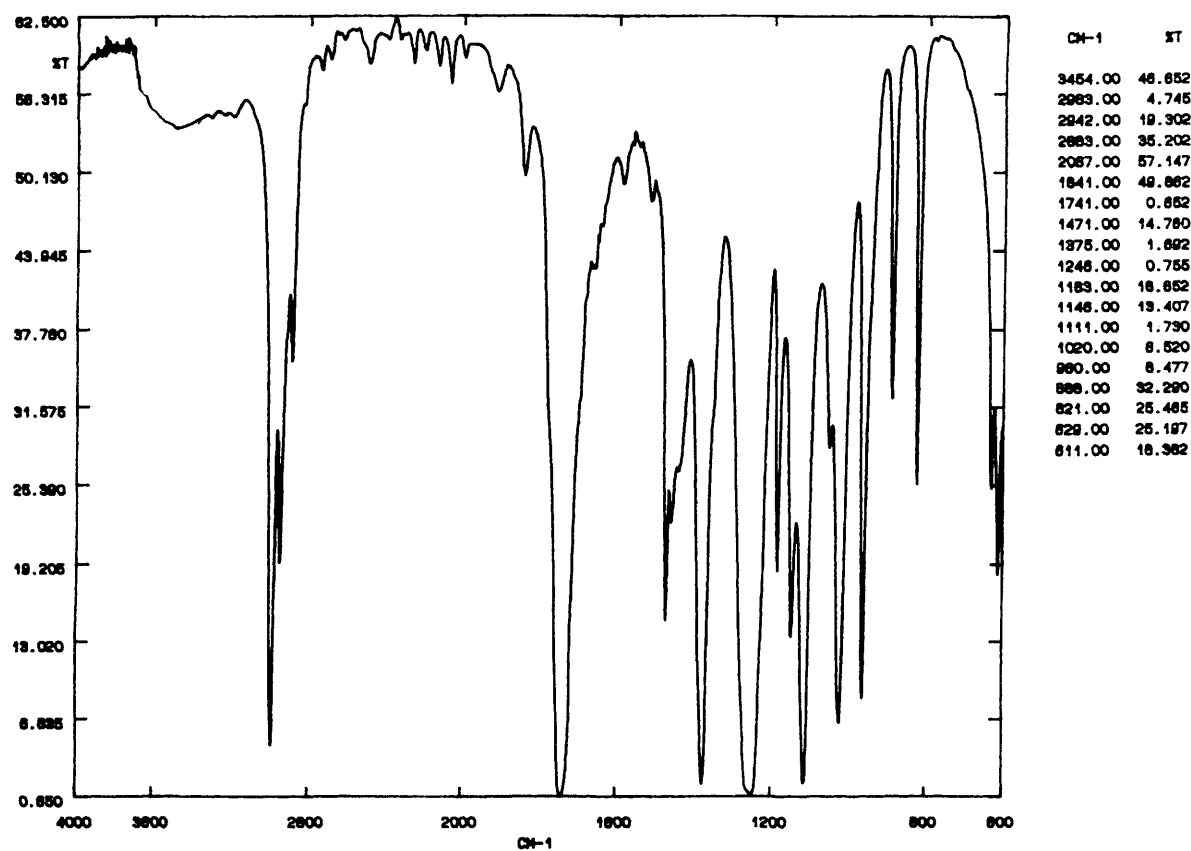
**DECOUPLED SPECTRUM****DEPT SPECTRUM**

Sample 5.10

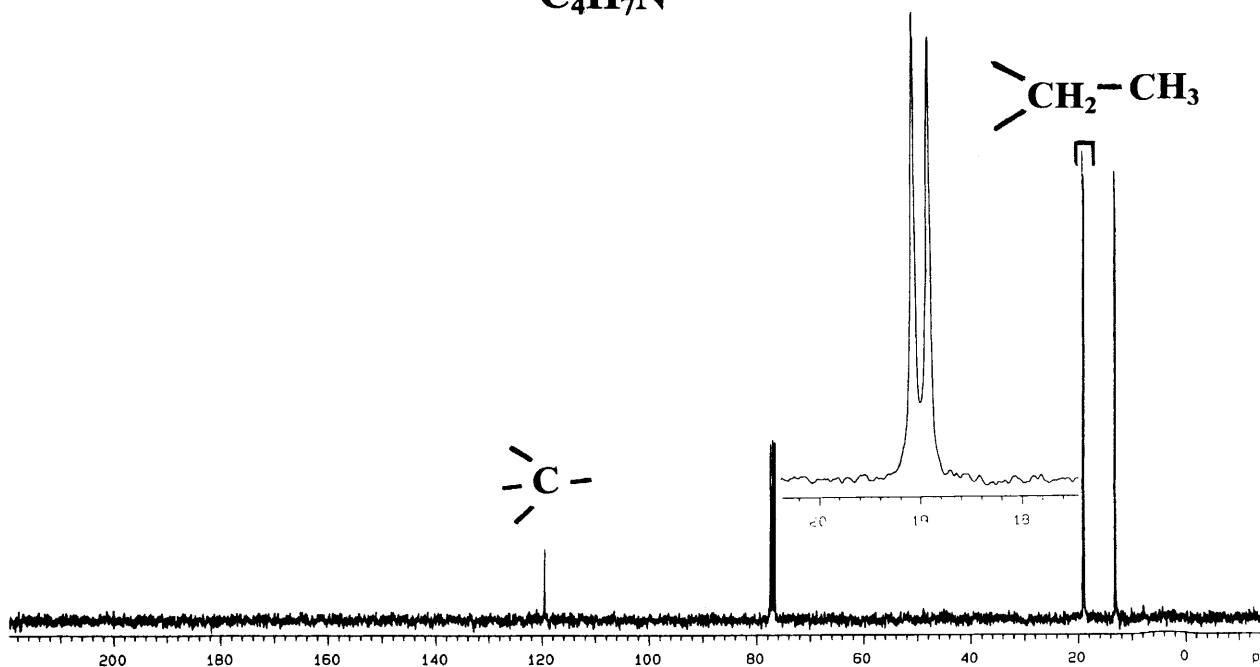
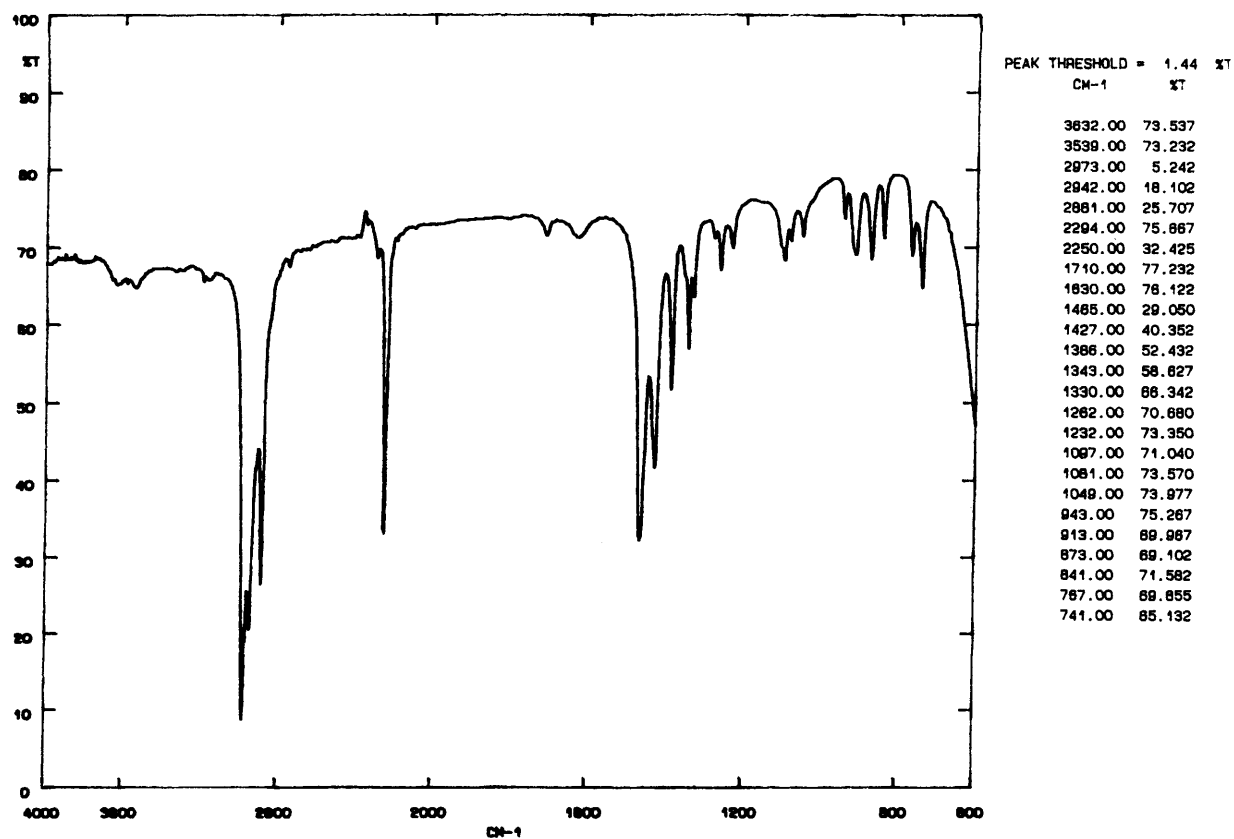
## Problems in Interpreting Infrared Spectra and $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra

In this chapter, as in all further chapters, only decoupled  $^{13}\text{C}$  NMR spectra are given. Instead of DEPT spectra, an indication of whether each peak represents C, CH,  $\text{CH}_2$  or  $\text{CH}_3$  is given on the decoupled spectrum.

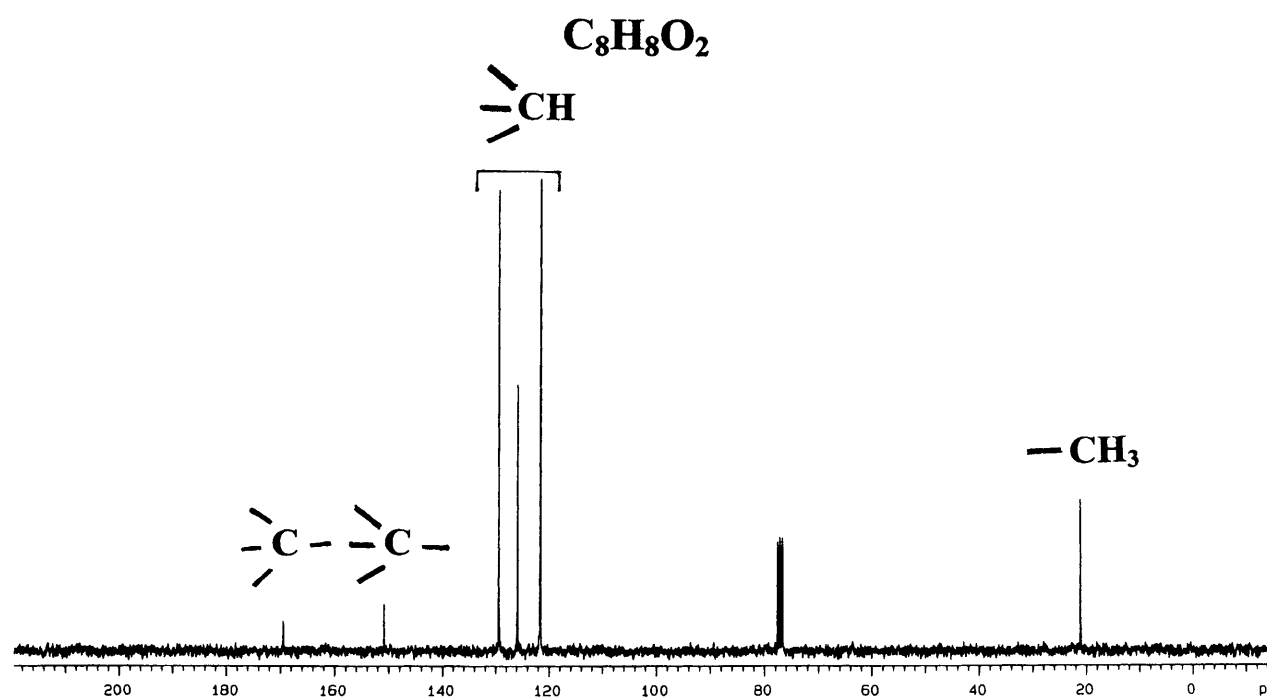
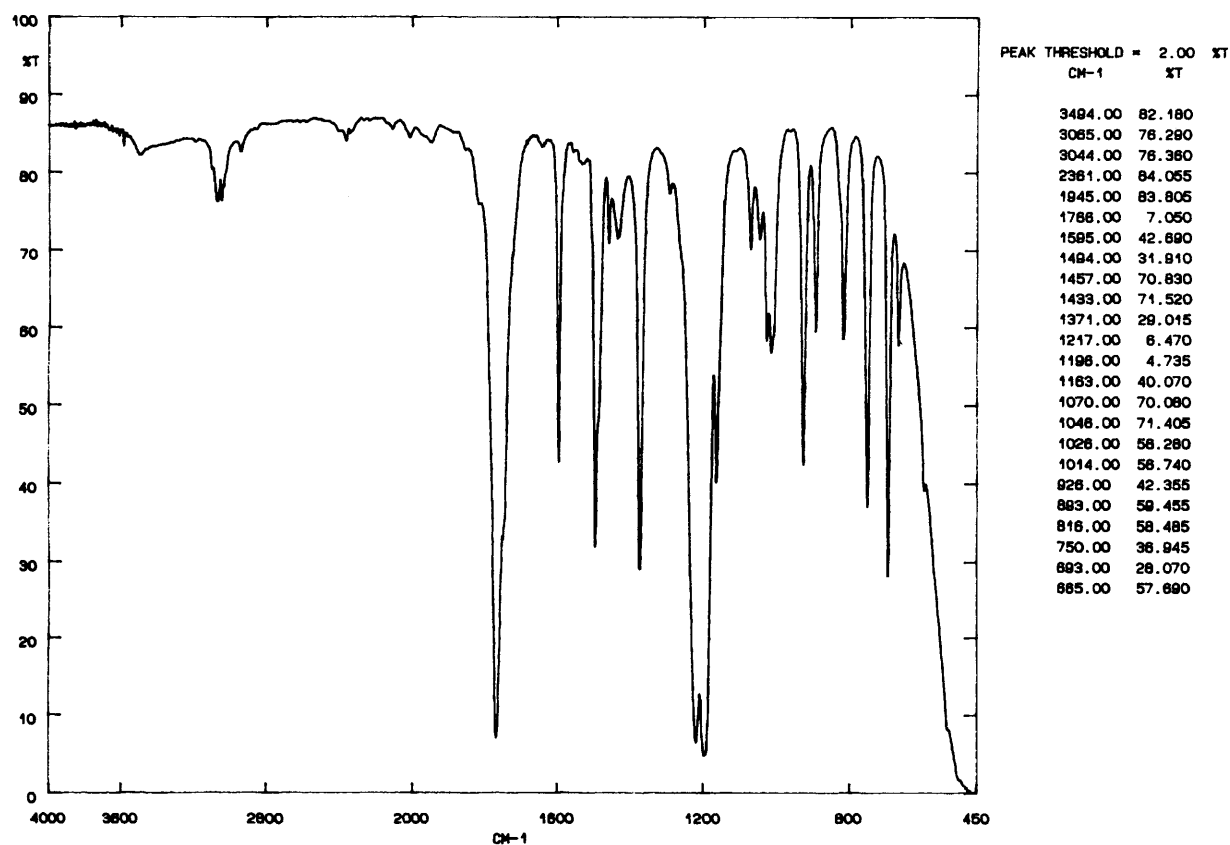
Combining infrared and  $^{13}\text{C}$  NMR spectra greatly extends the range of compounds that we can identify. We still need molecular formulae, and these are provided. Although we can identify some functional groups by  $^{13}\text{C}$  NMR, infrared is a better technique for all except alkenes and aromatic rings which sometimes have small infrared peaks but are easily seen by  $^{13}\text{C}$  NMR. The carbonyl group in particular should always be examined by infrared spectroscopy, and the two techniques supplement each other when identifying alkyne and nitrile groups.



Sample 6.1

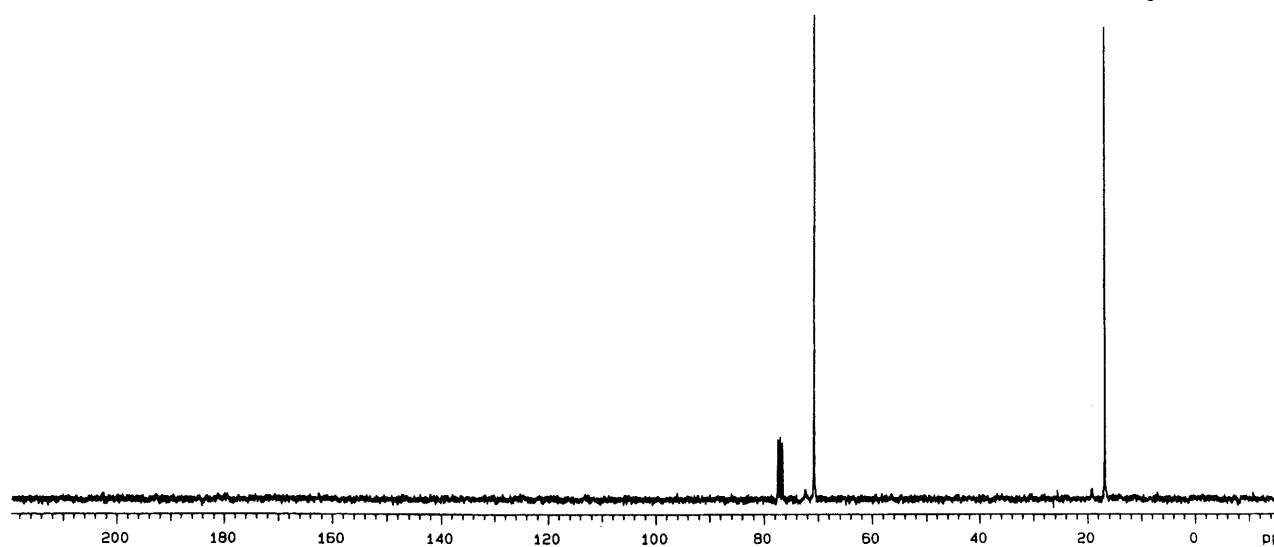
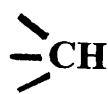
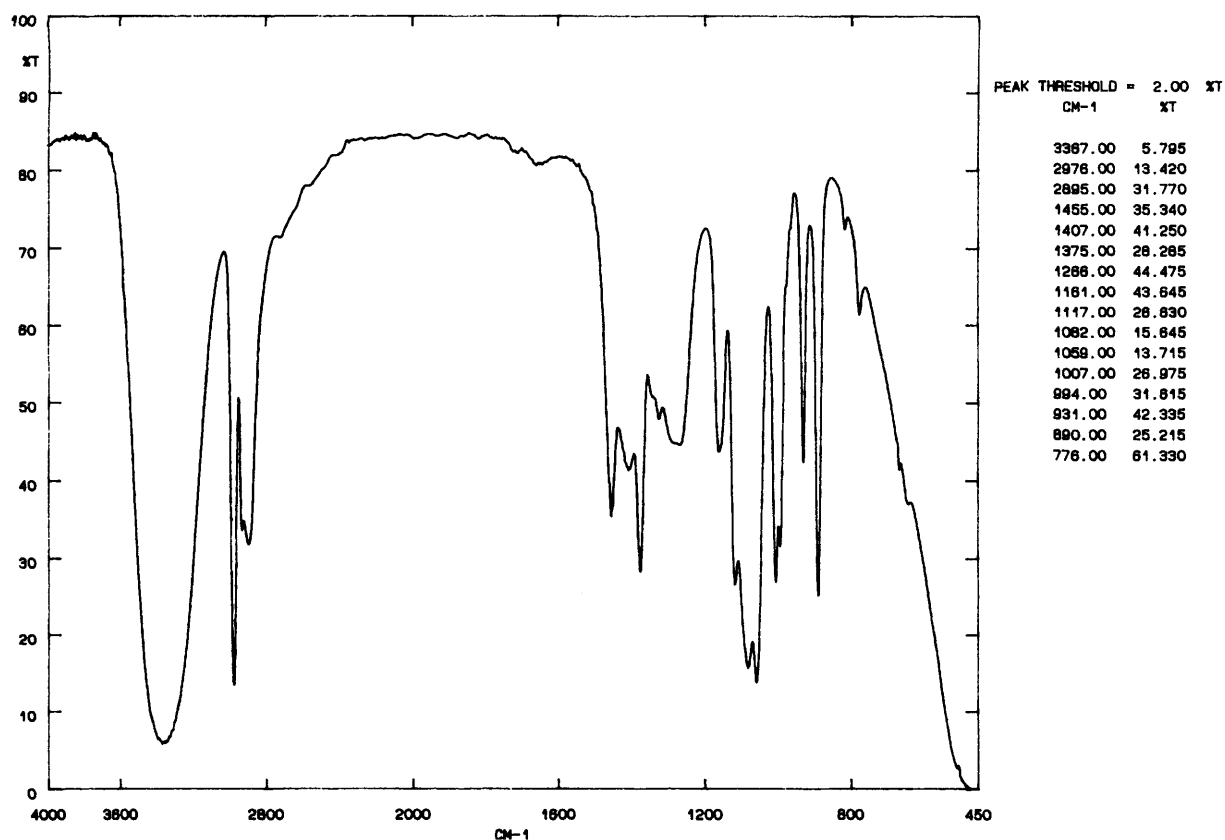


Sample 6.2

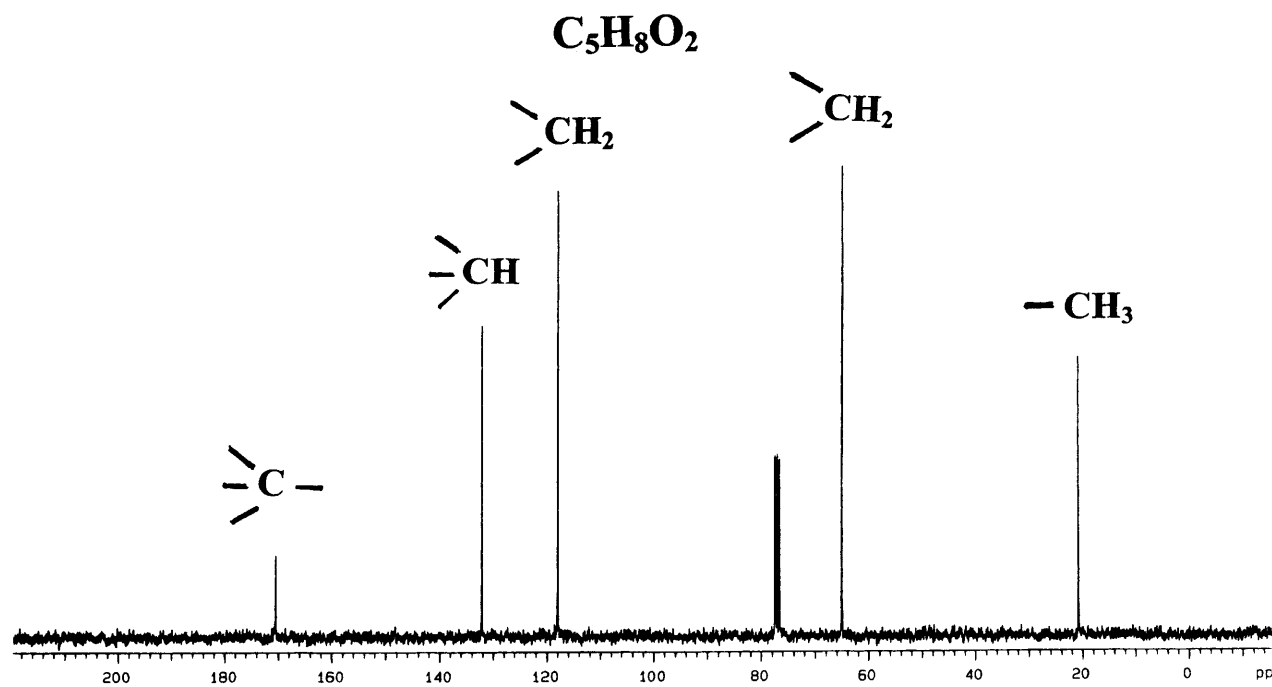
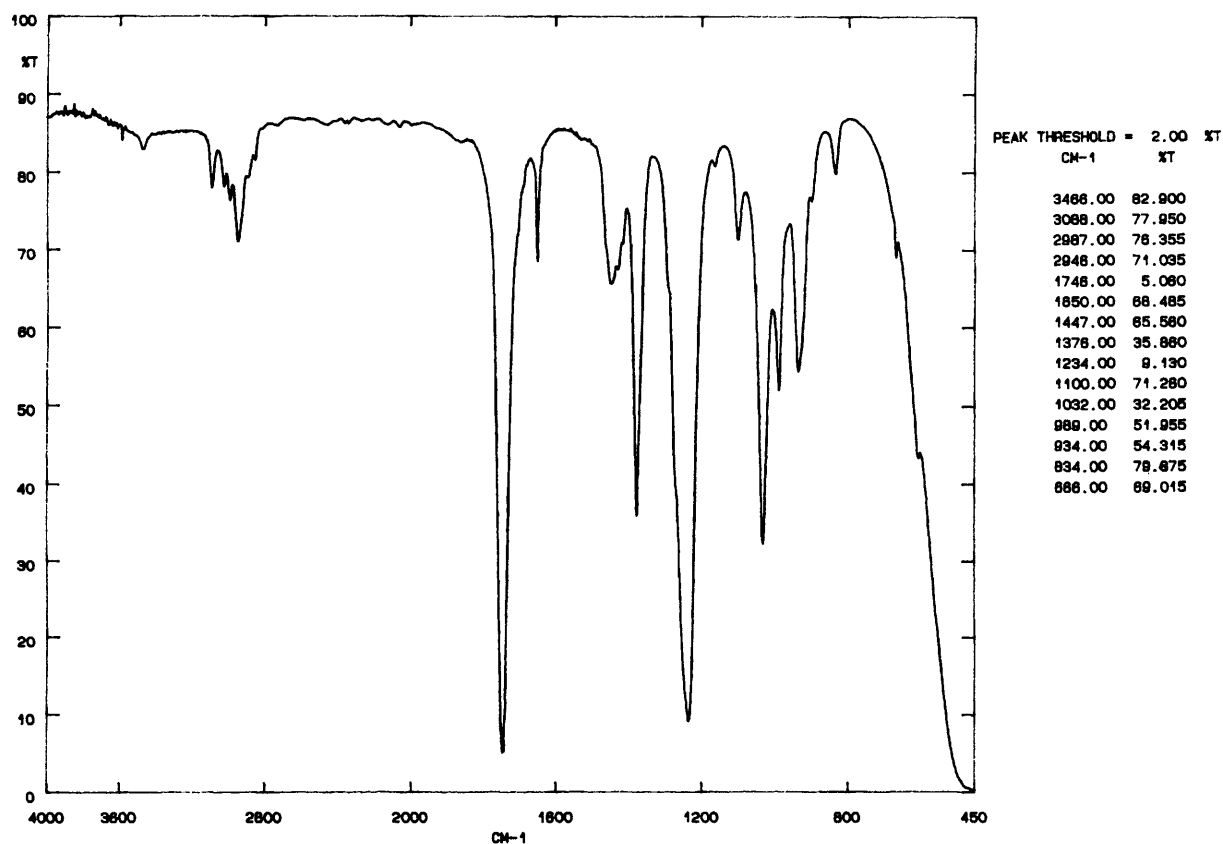


Sample 6.3

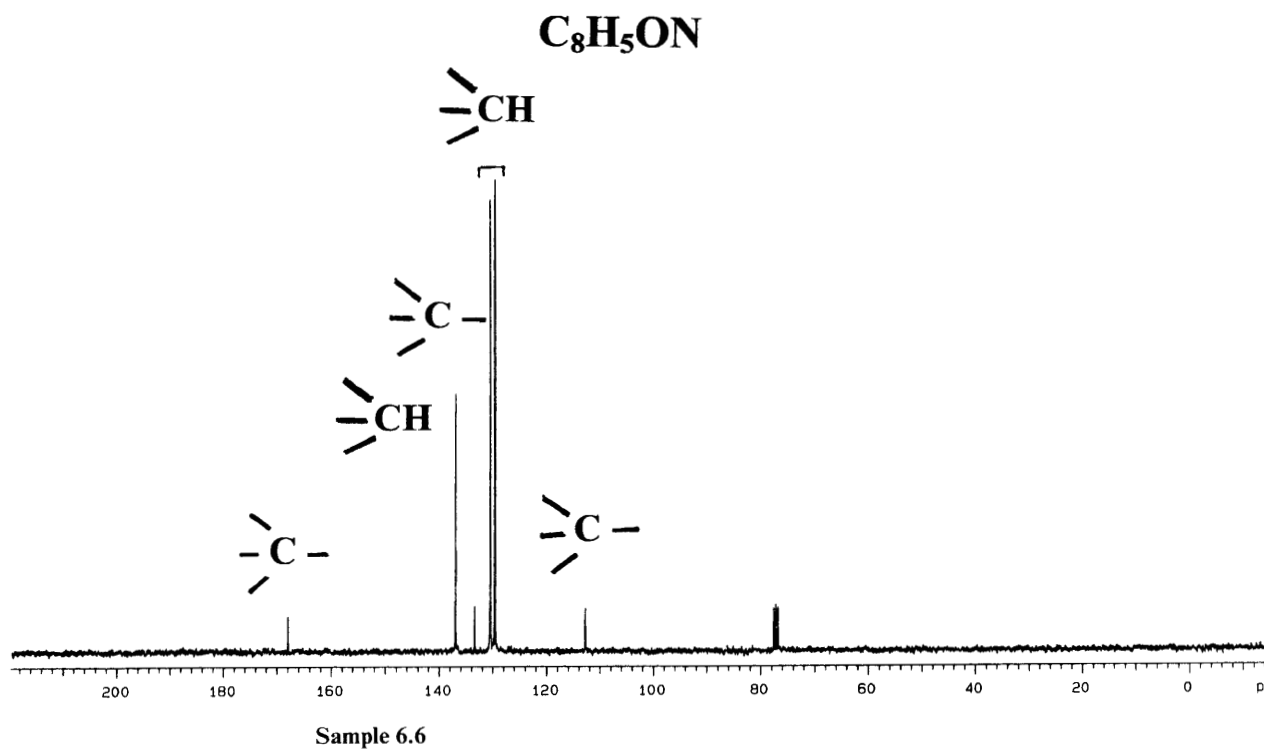
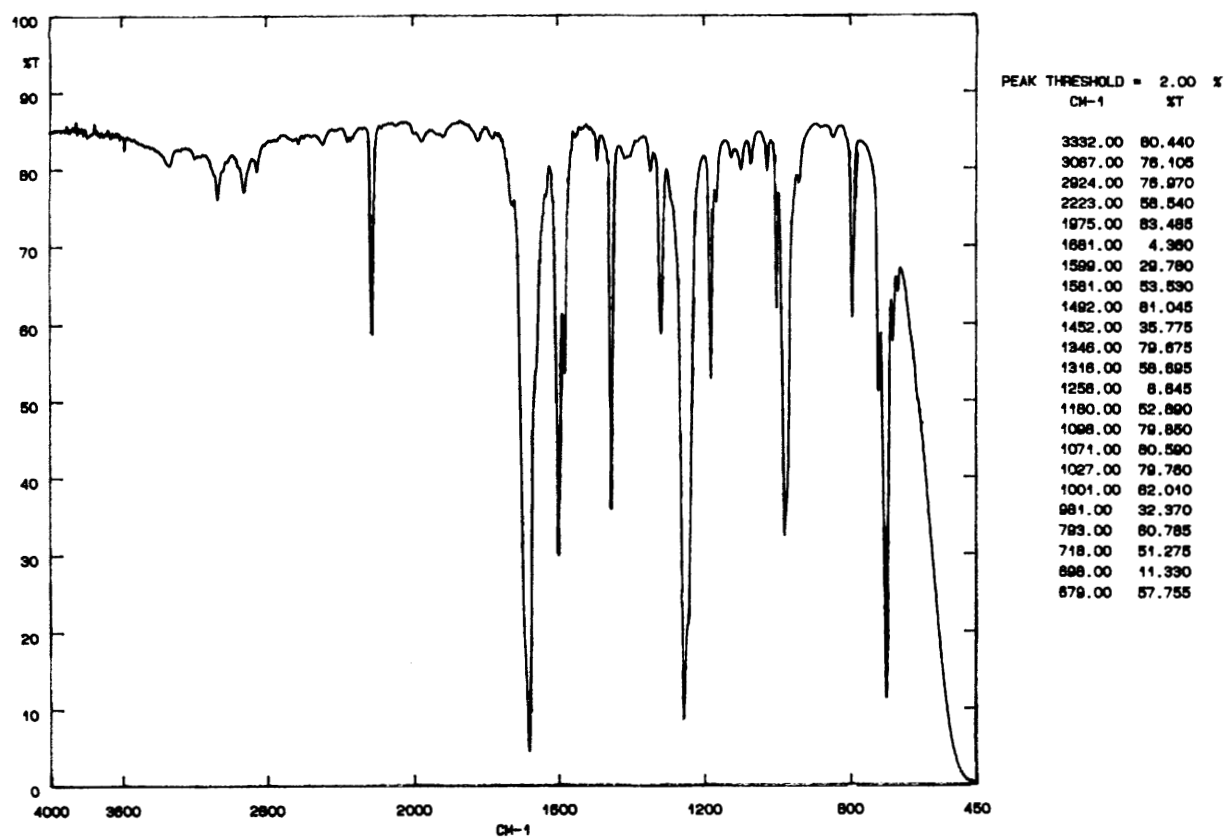


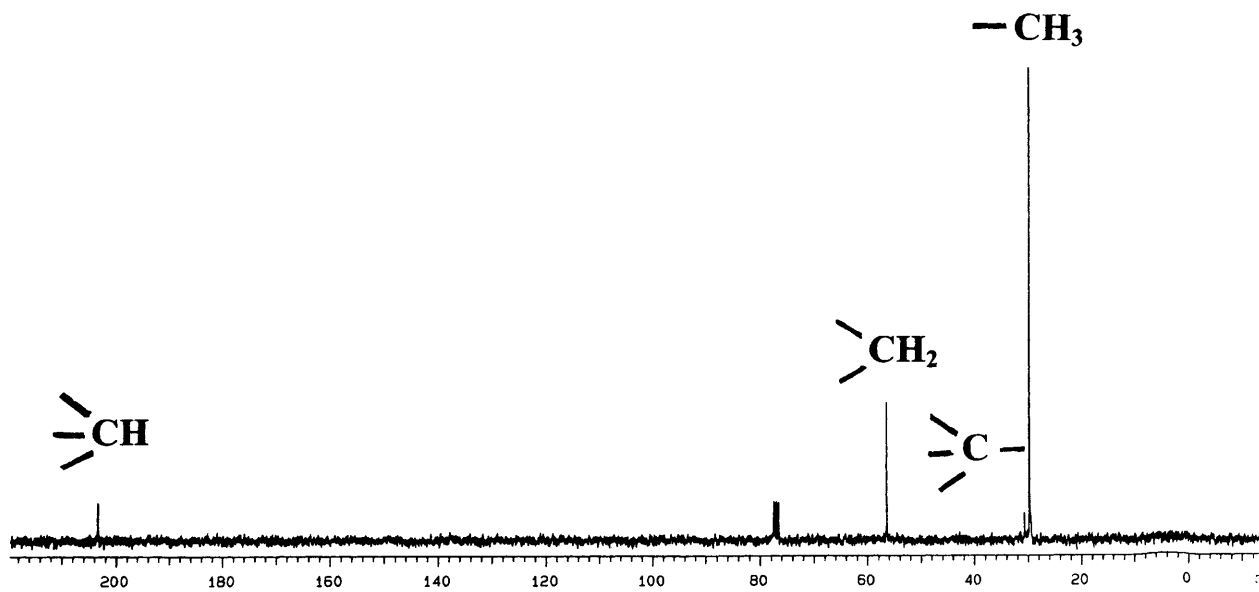
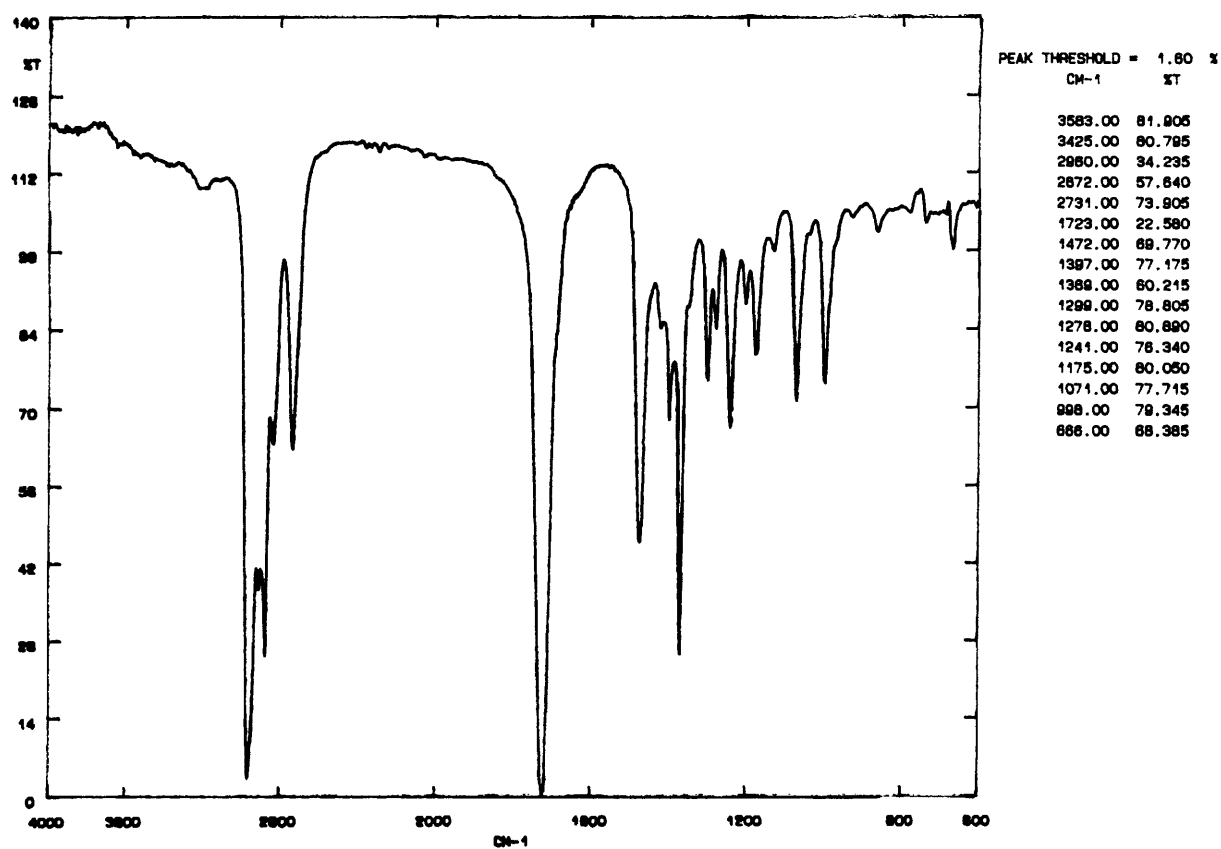


Sample 6.4

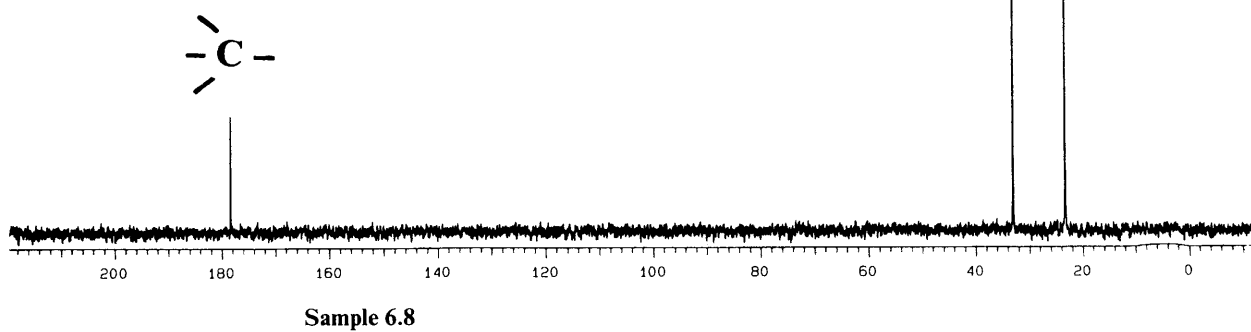
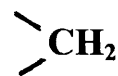
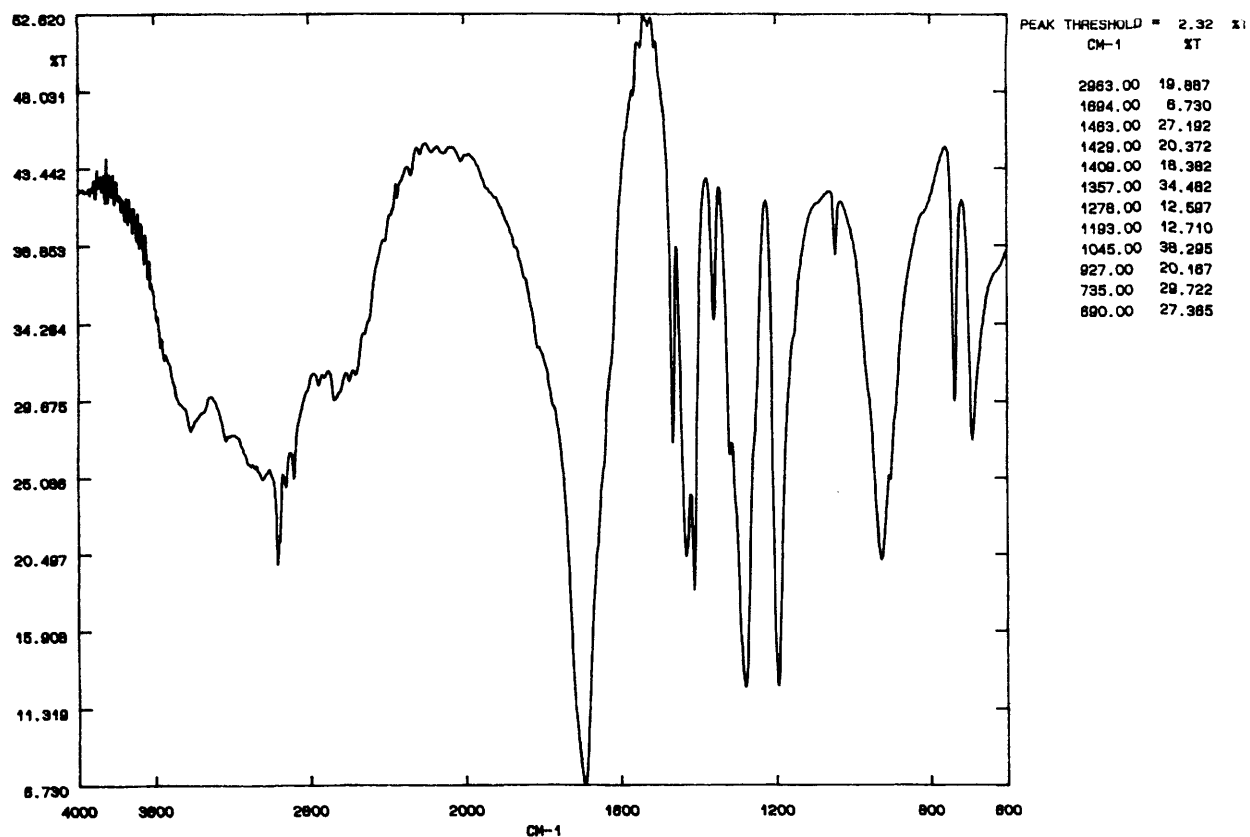


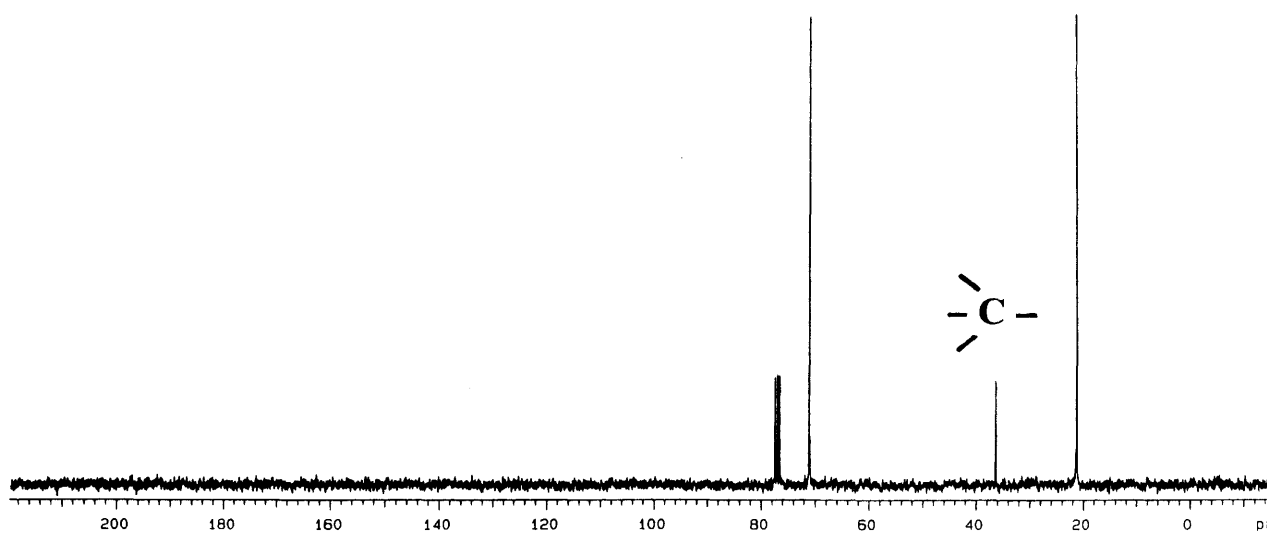
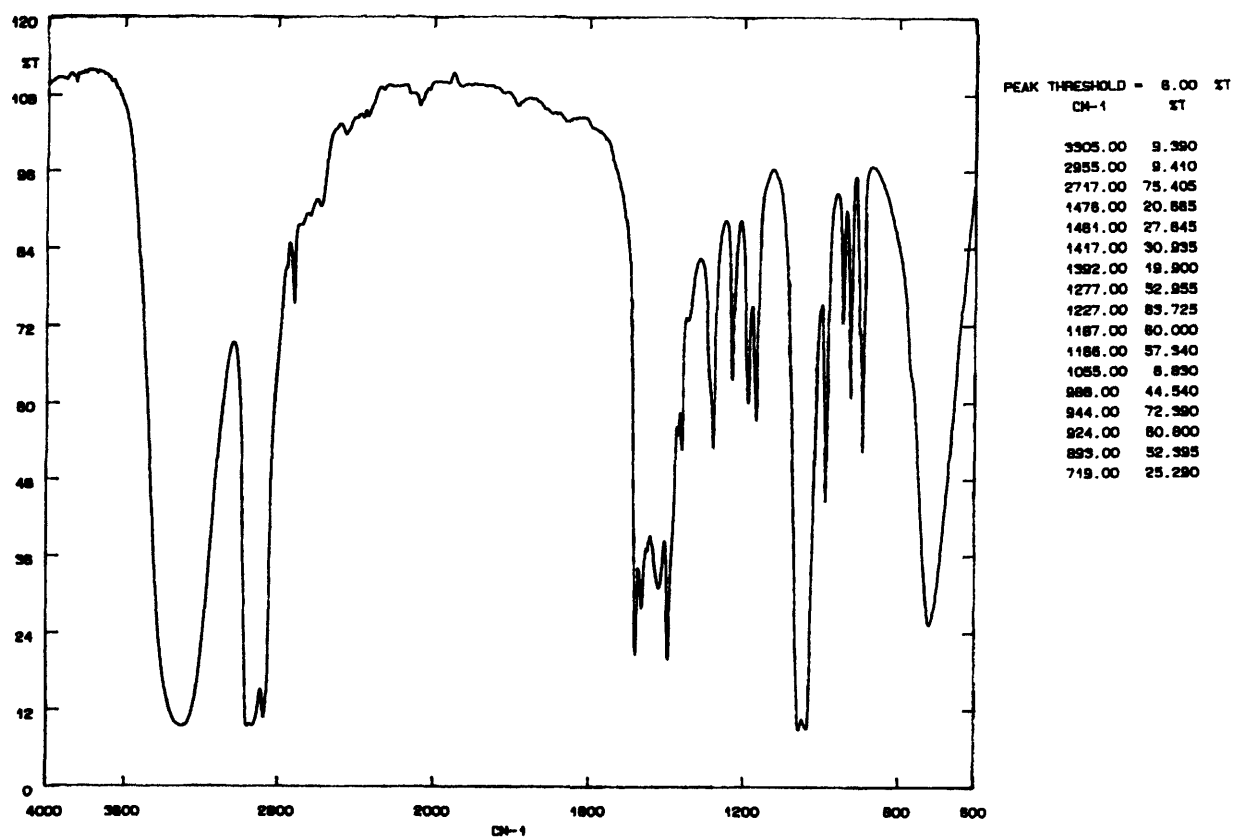
Sample 6.5



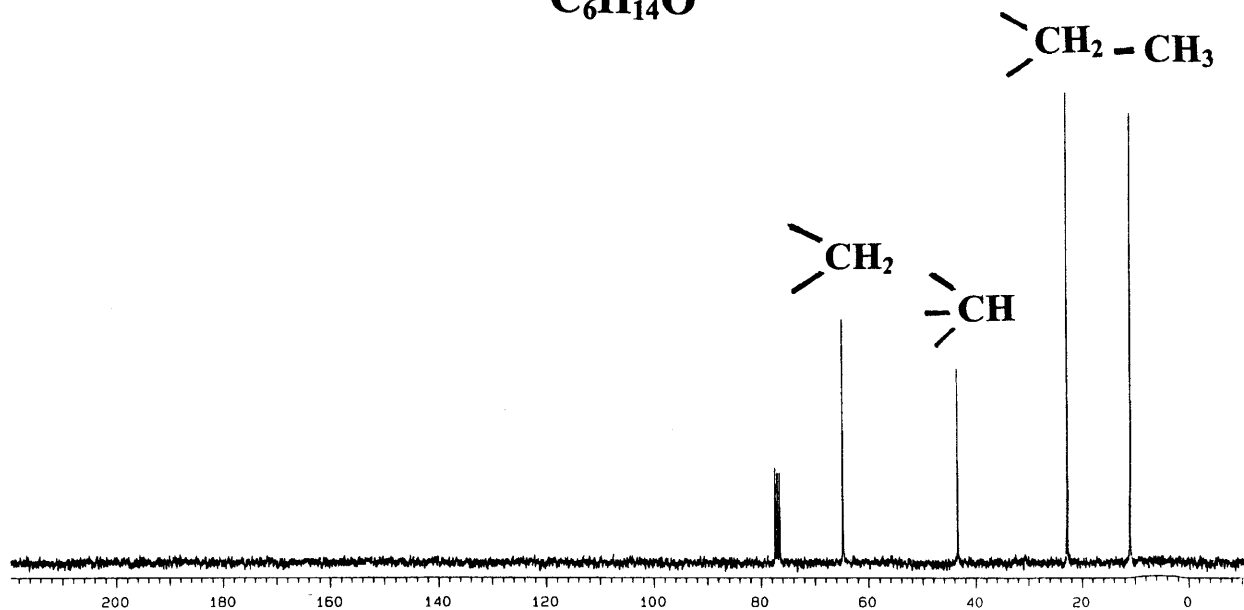
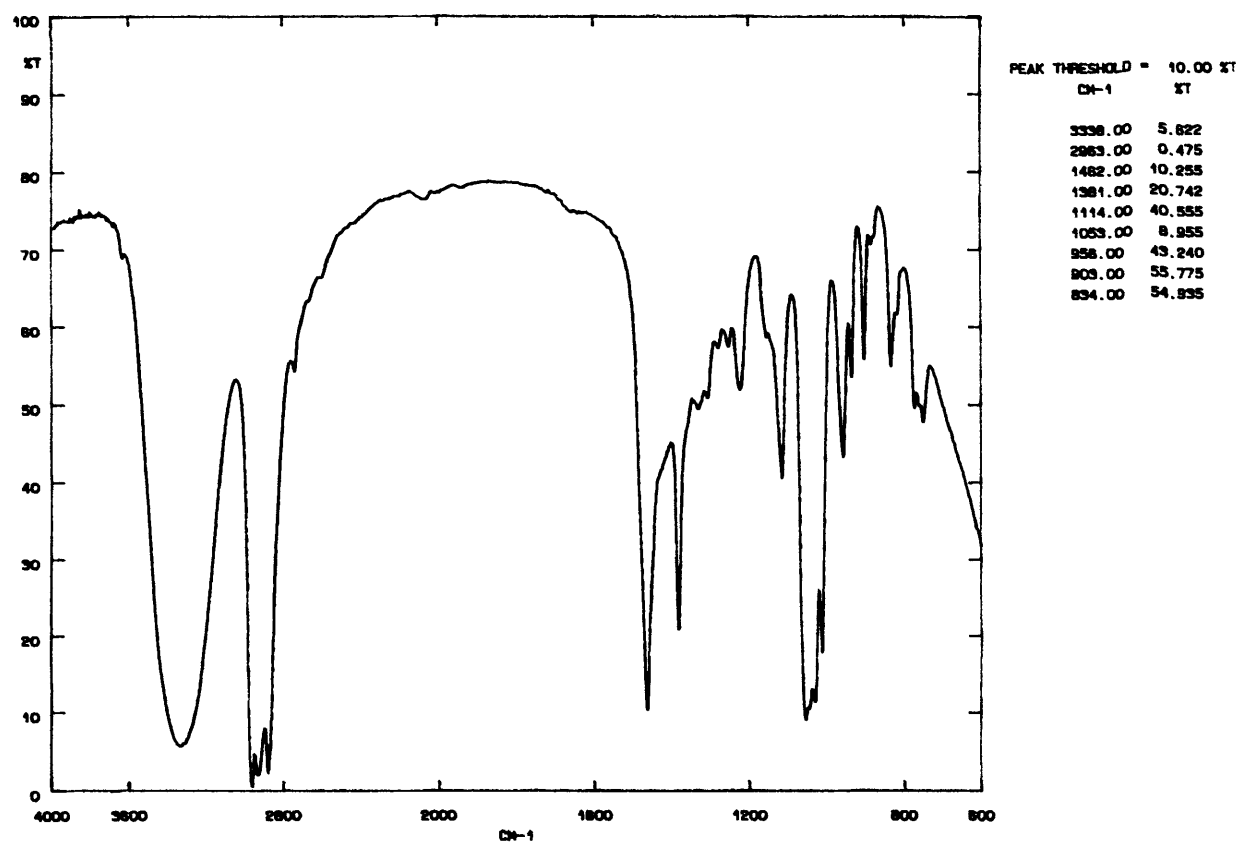


Sample 6.7





Sample 6.9



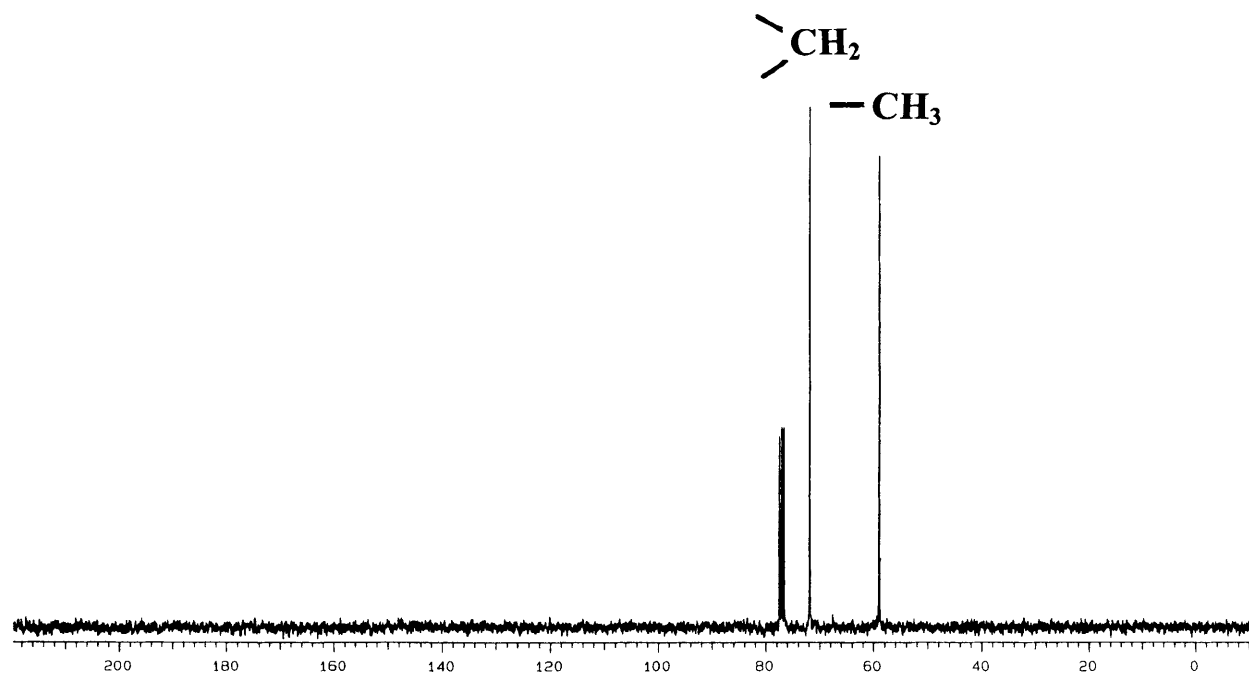
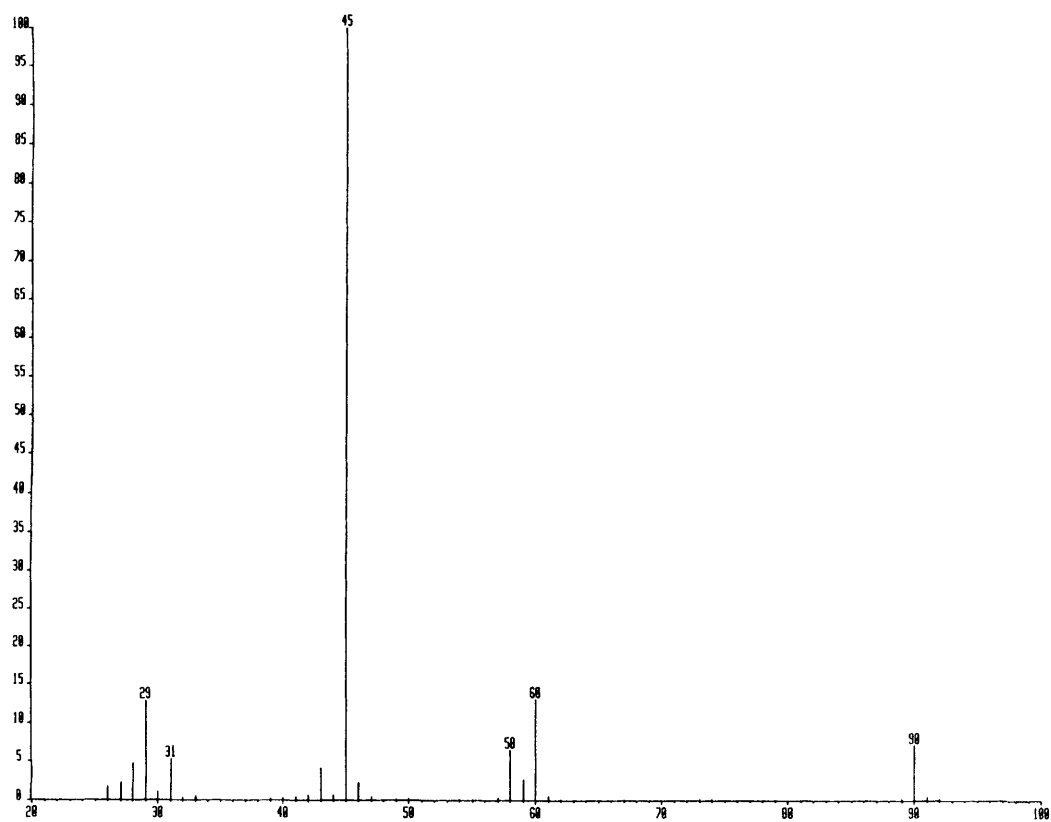
Sample 6.10



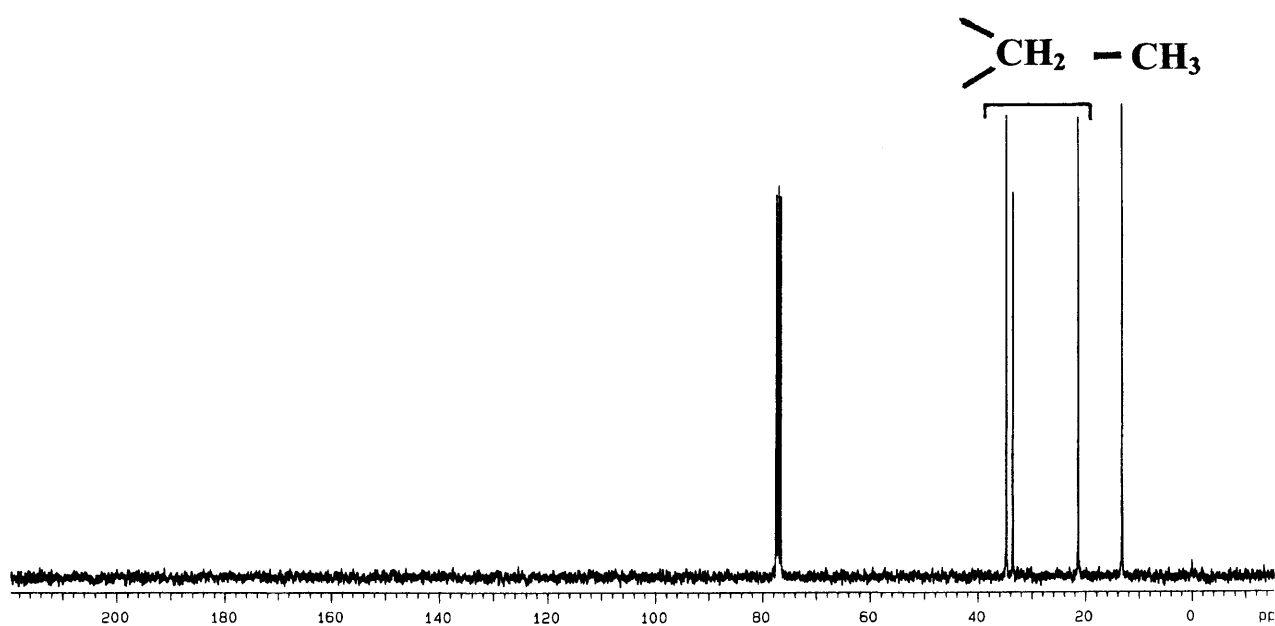
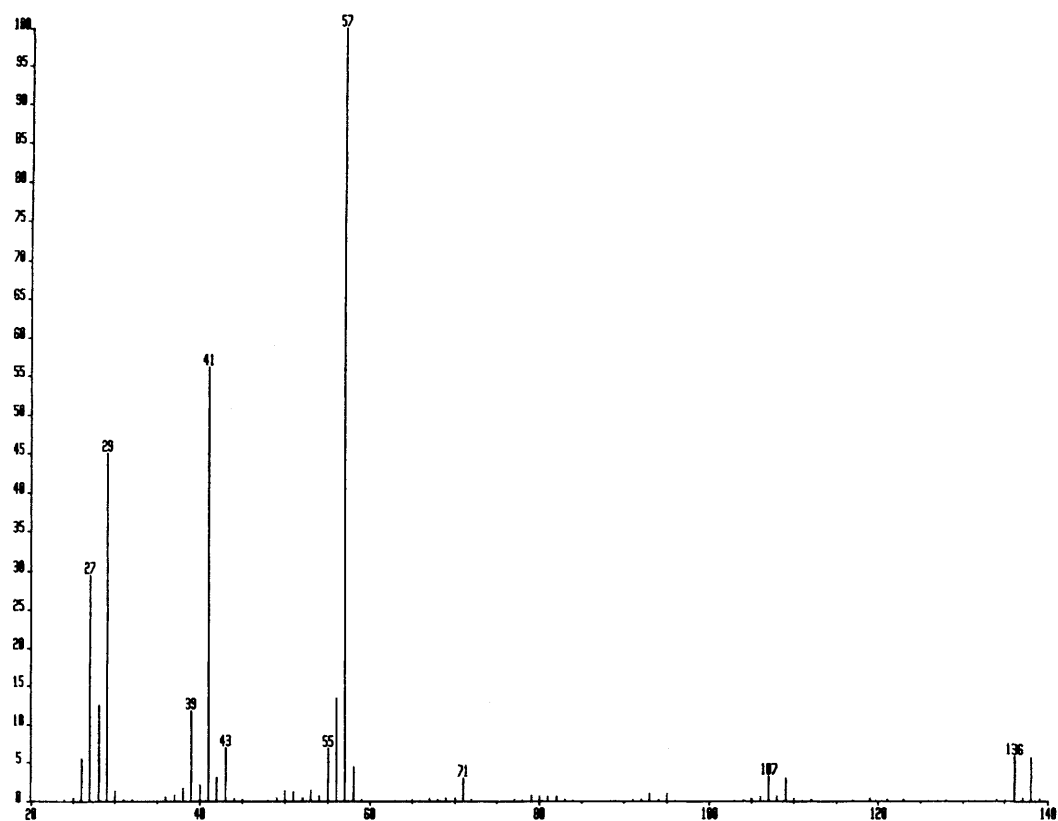


## **Problems in Interpreting Mass Spectra and $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra**

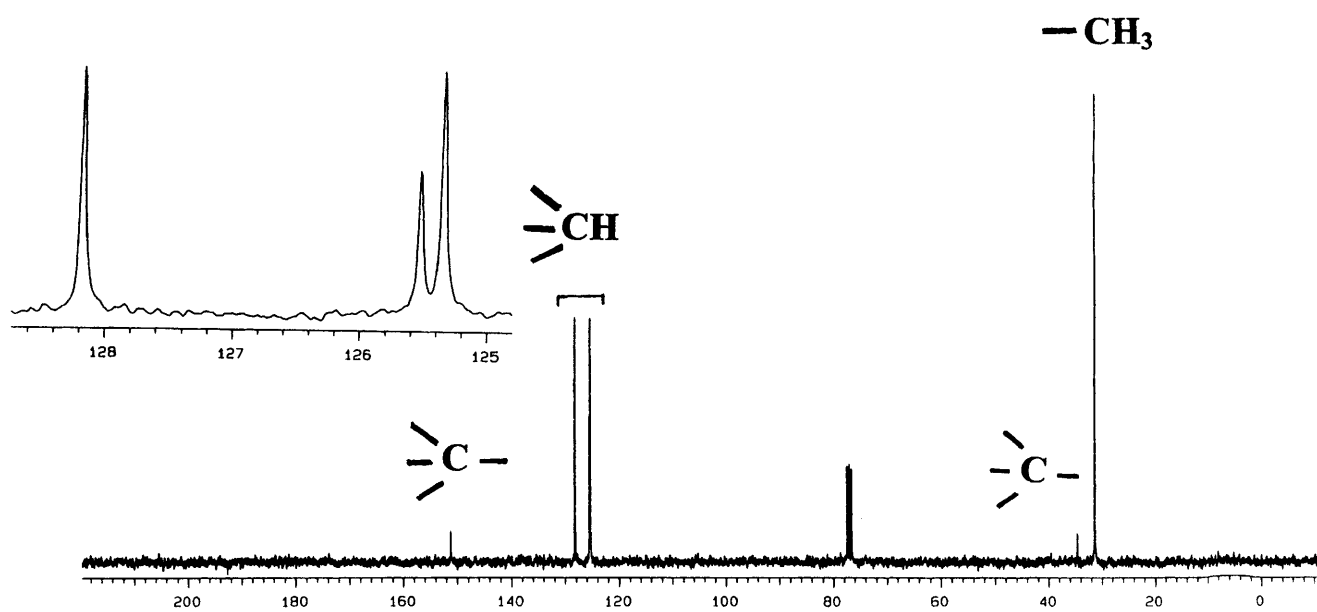
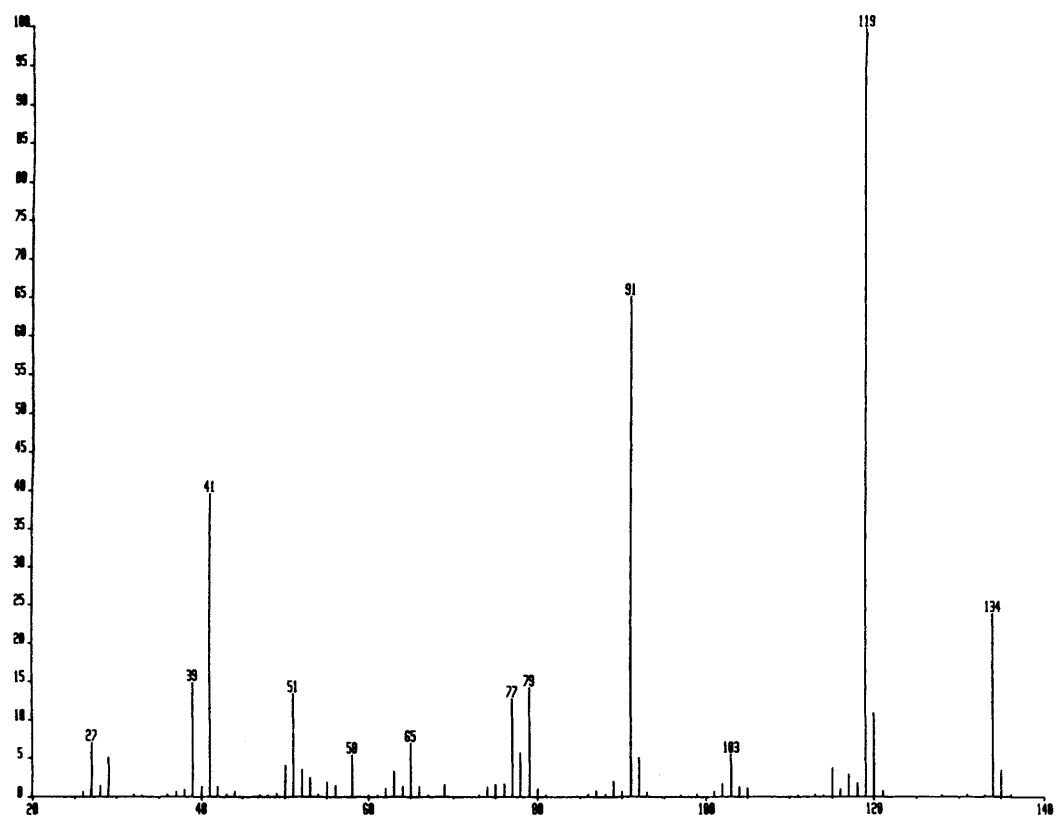
In this chapter, we combine mass spectra with  $^{13}\text{C}$  NMR spectra, so we no longer need molecular formulae. The techniques again complement each other; minimally, mass spectra give us the molecular weight and the halogen content, while  $^{13}\text{C}$  NMR gives us carbonyl groups, double bonds, aromatic rings, alkyne and nitrile groups. Both techniques can contribute a lot more than this to a structure. Mass spectra can tell us of the presence of nitrogen (tertiary amines are otherwise very difficult to detect) and a McLafferty rearrangement can give complete identification by itself in a few cases. The  $^{13}\text{C}$  NMR spectrum can identify individual carbon atoms, and mass spectra may then be able to say if a  $\text{CH}_3$  is part of an ethyl, propyl or butyl group. The method is particularly useful for identifying symmetrical and cyclic structures.



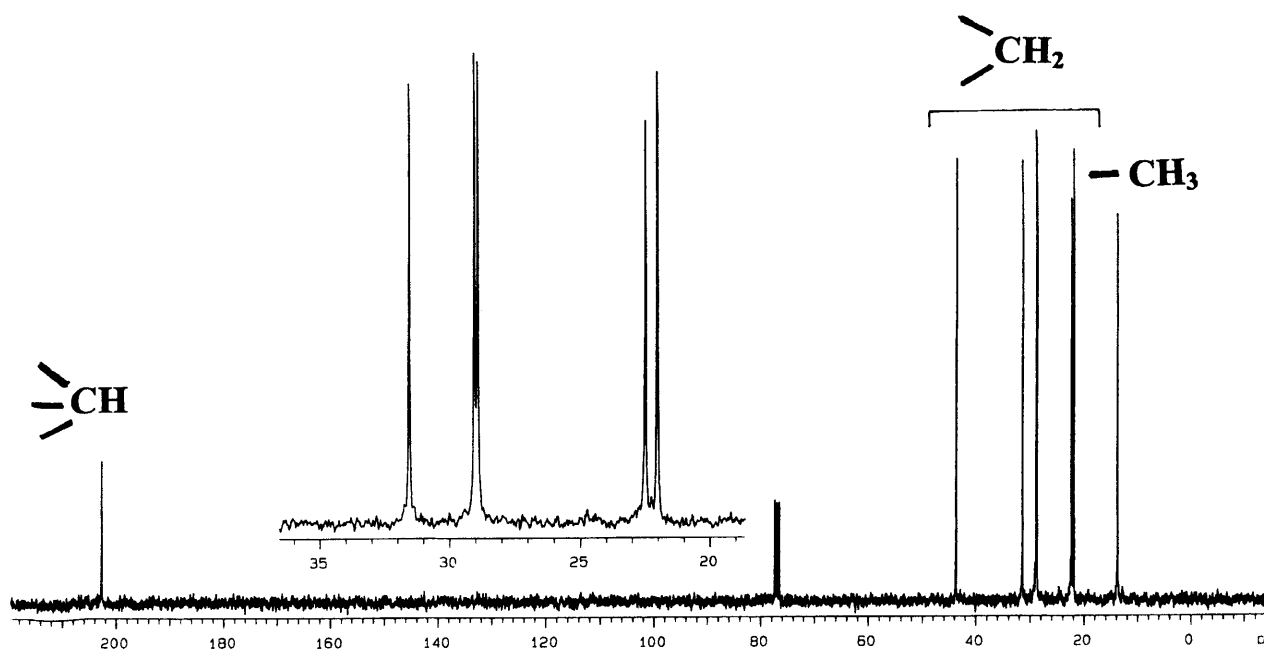
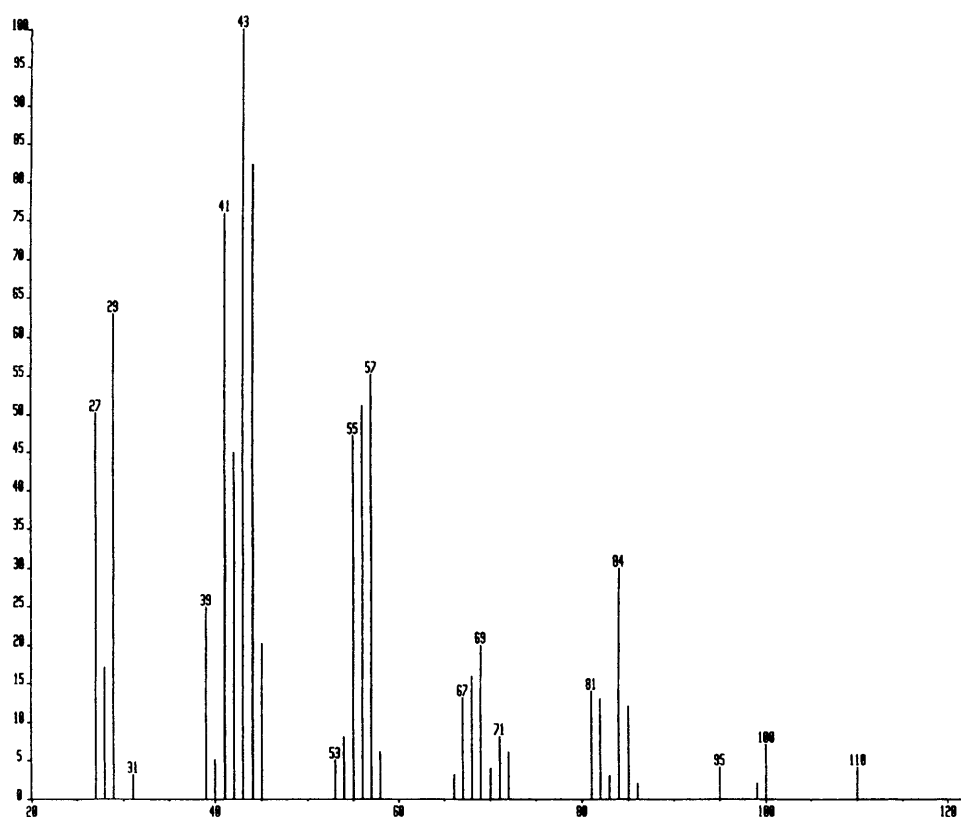
Sample 7.1



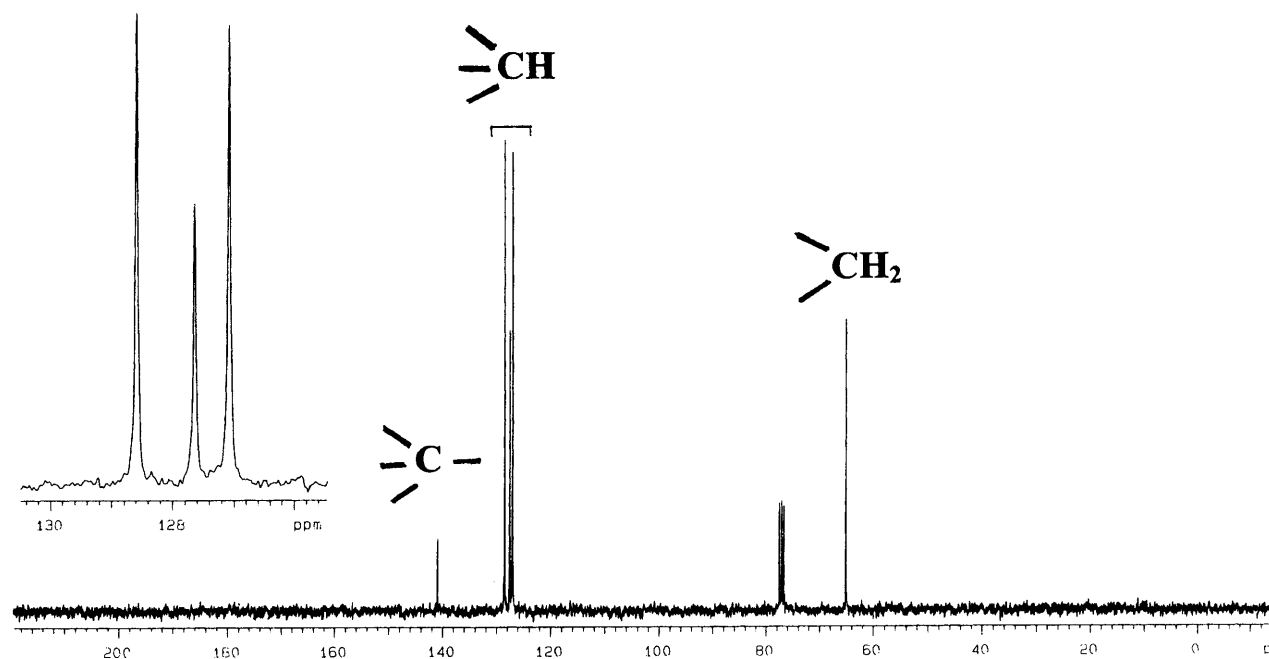
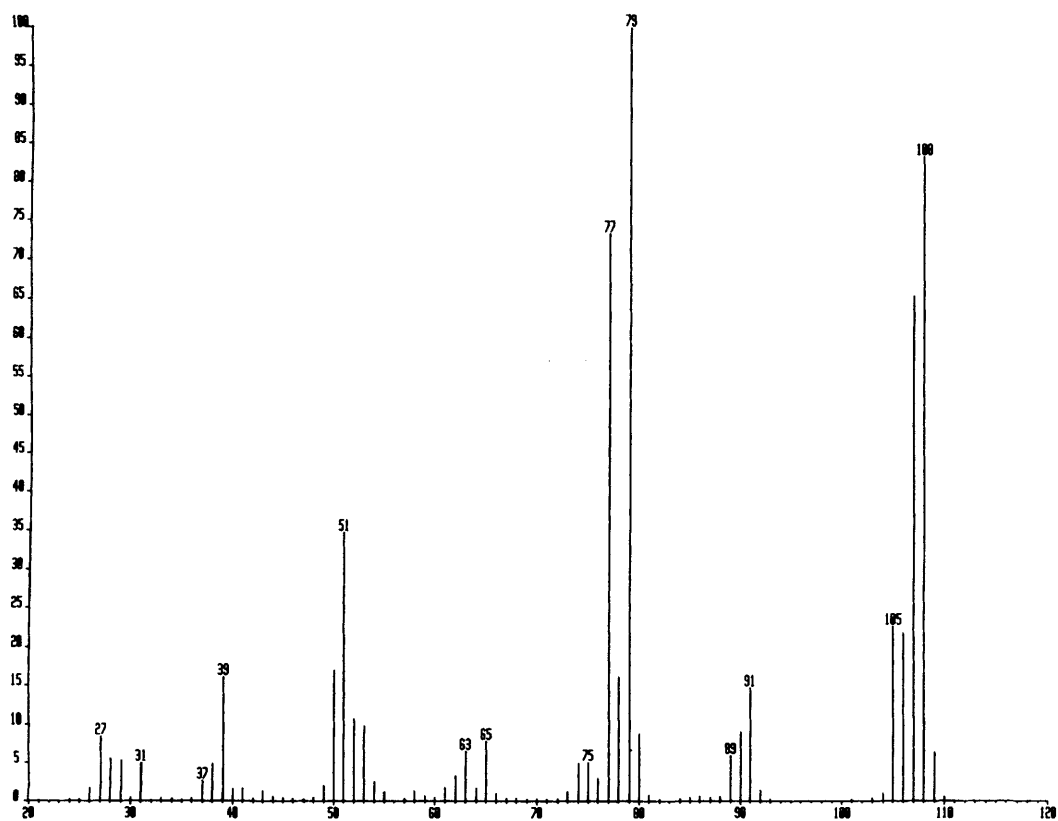
Sample 7.2



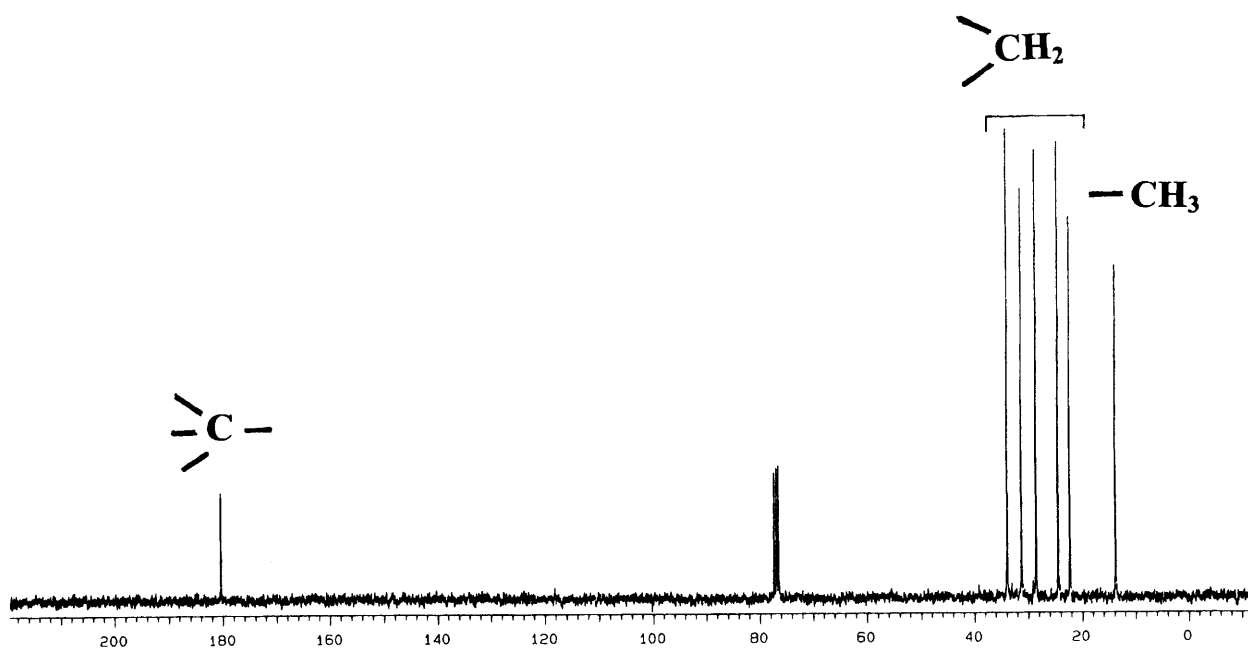
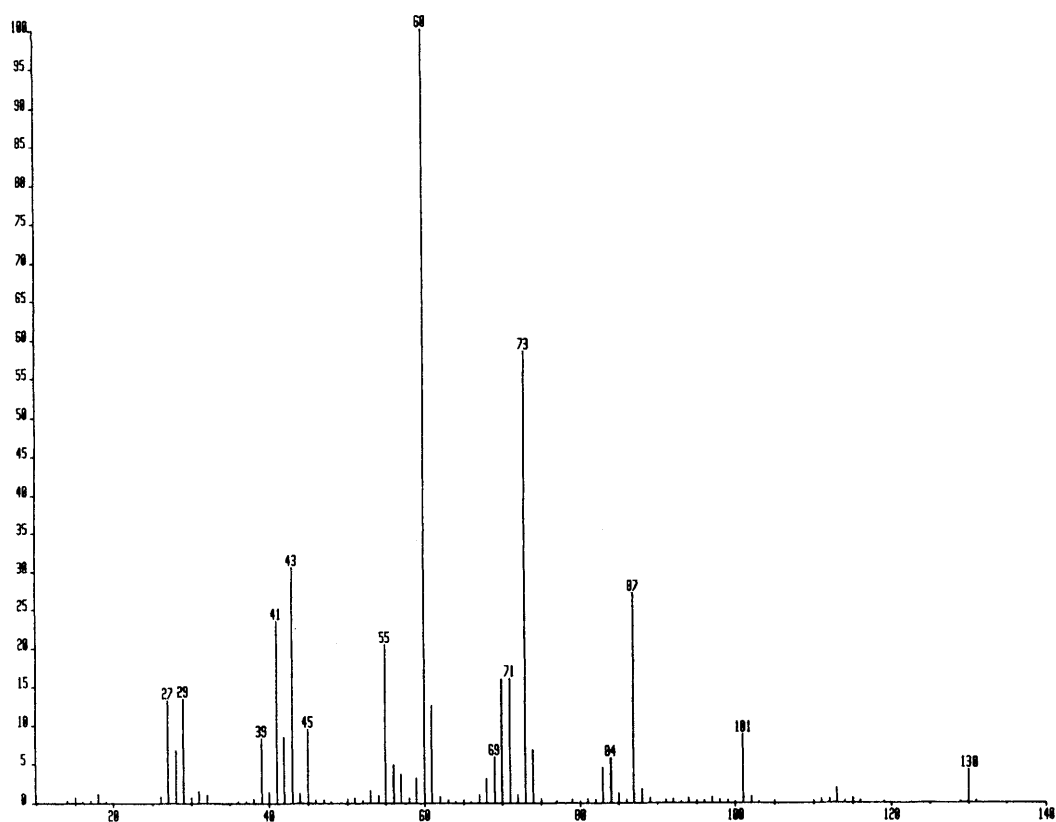
Sample 7.3



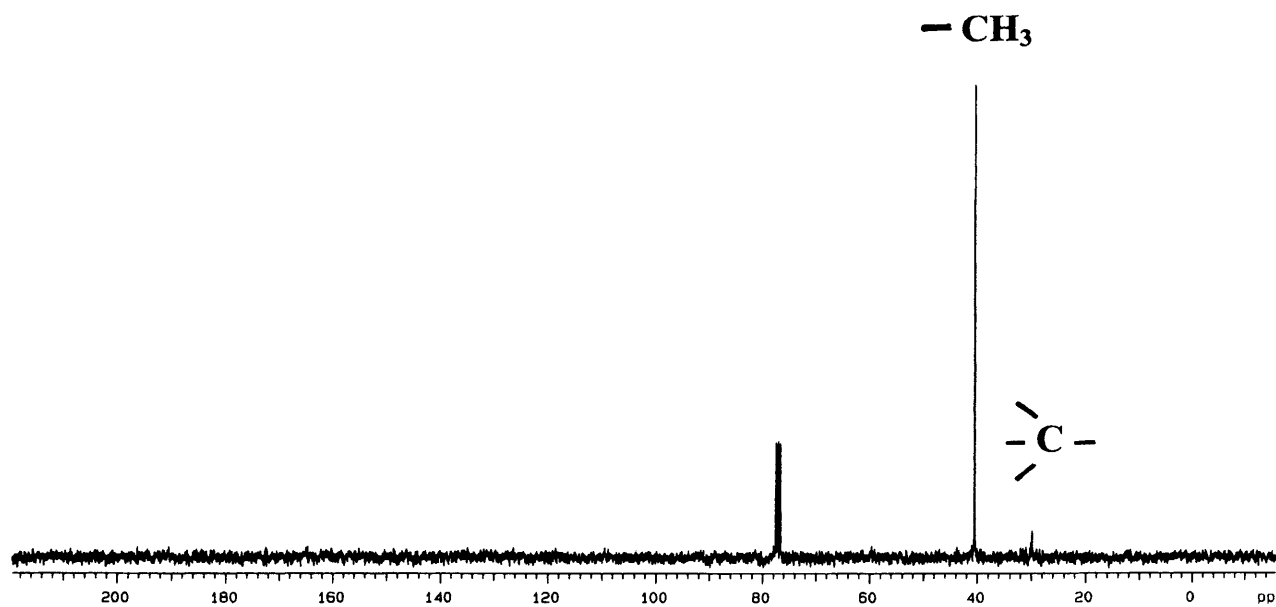
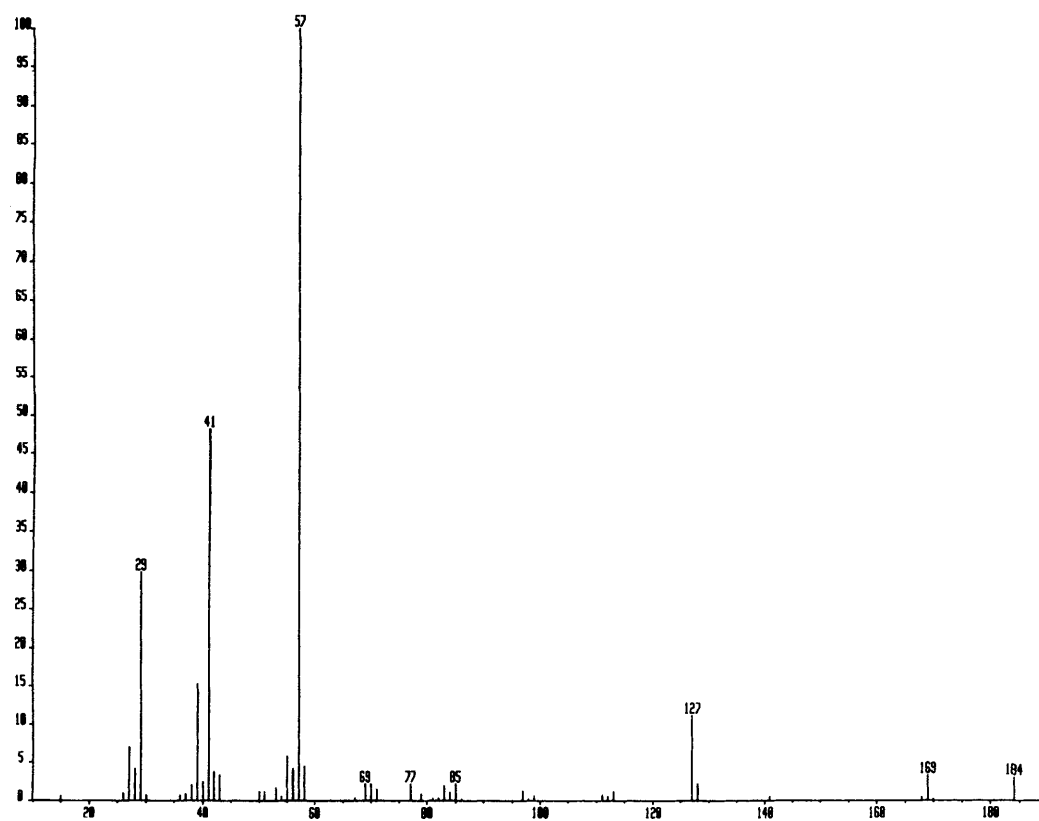
Sample 7.4



Sample 7.5

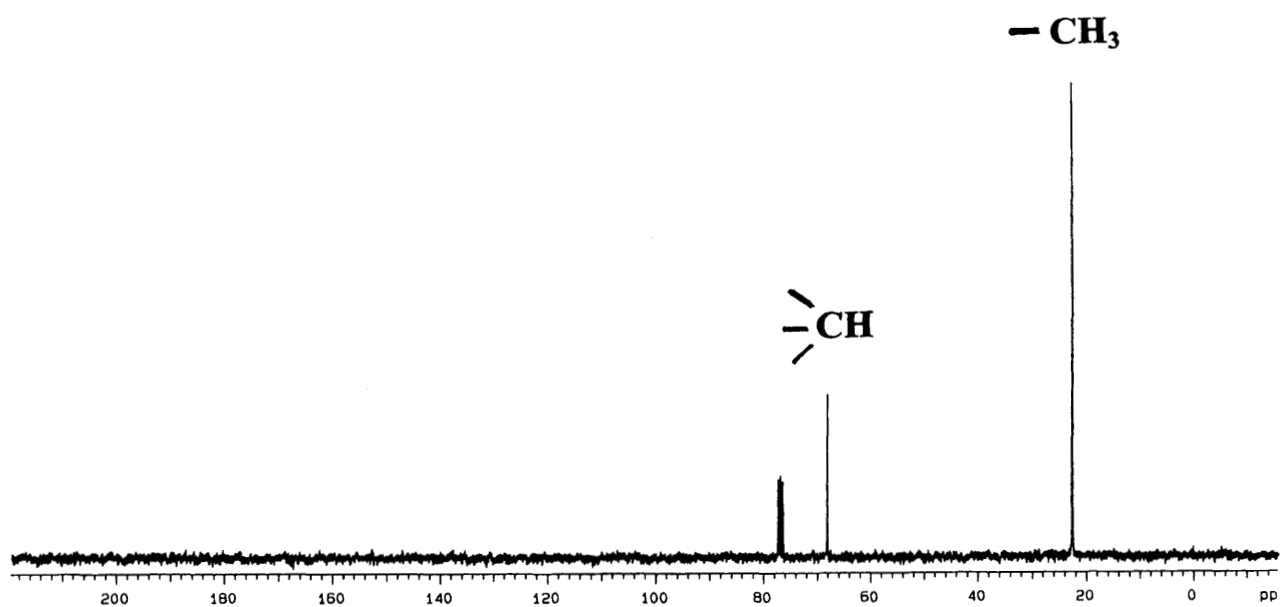
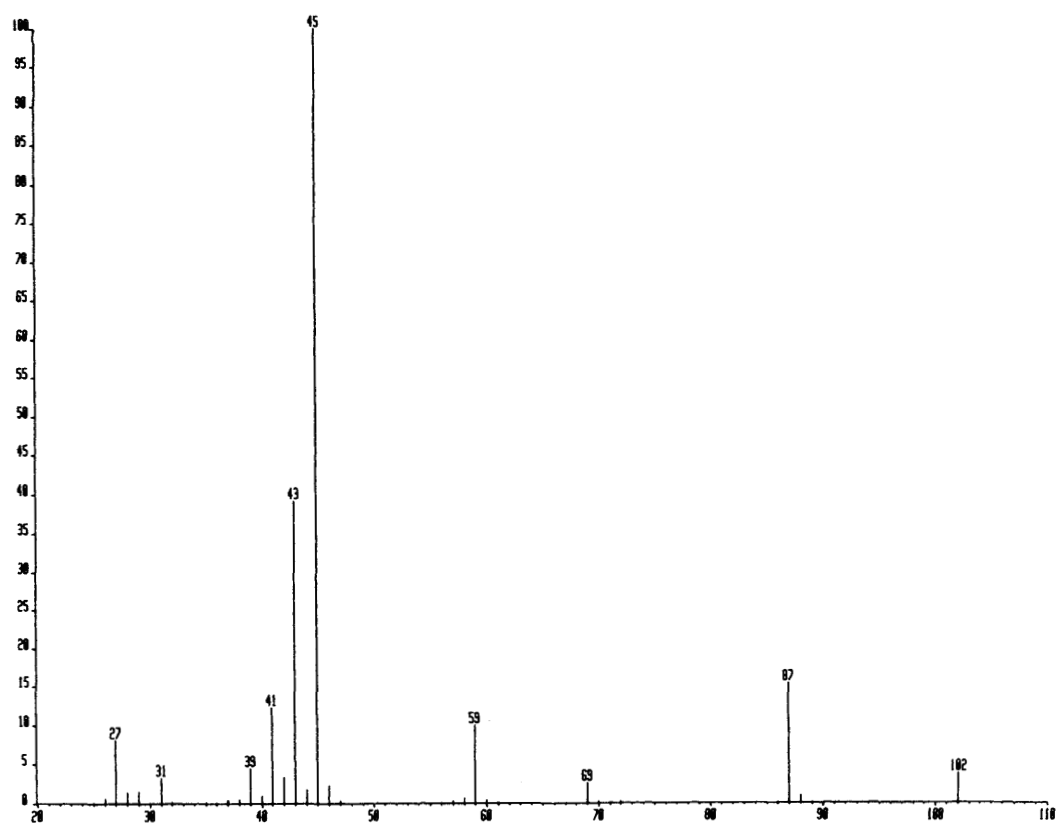


Sample 7.6

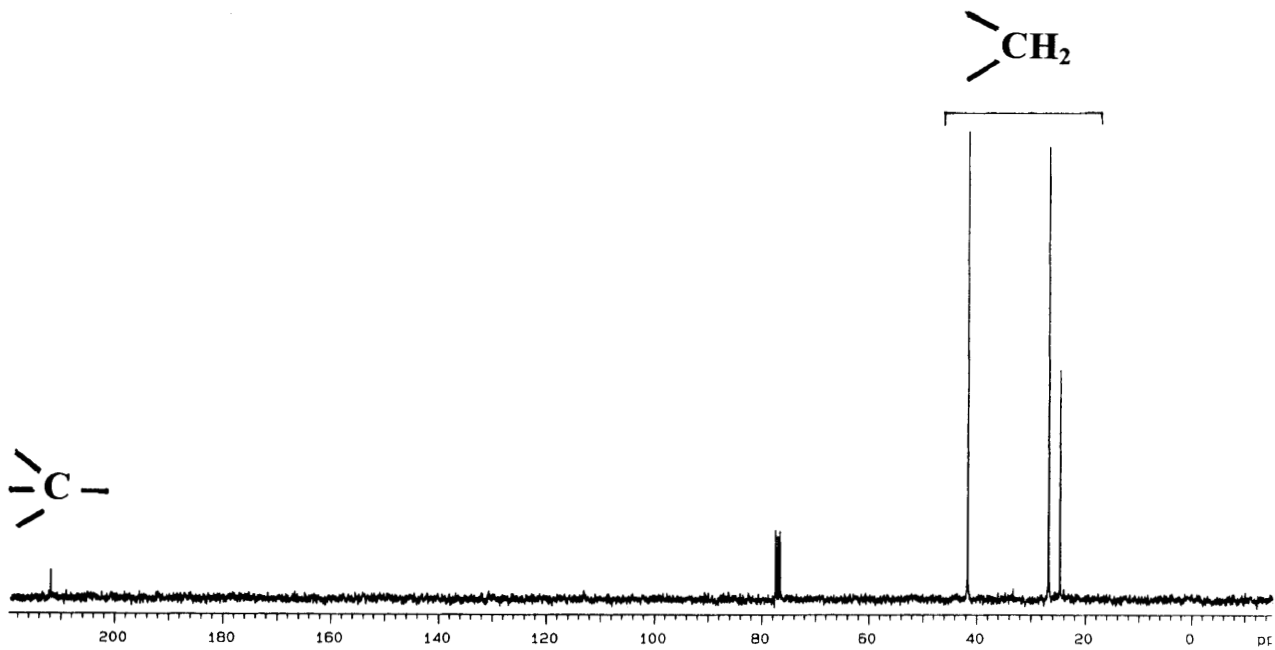
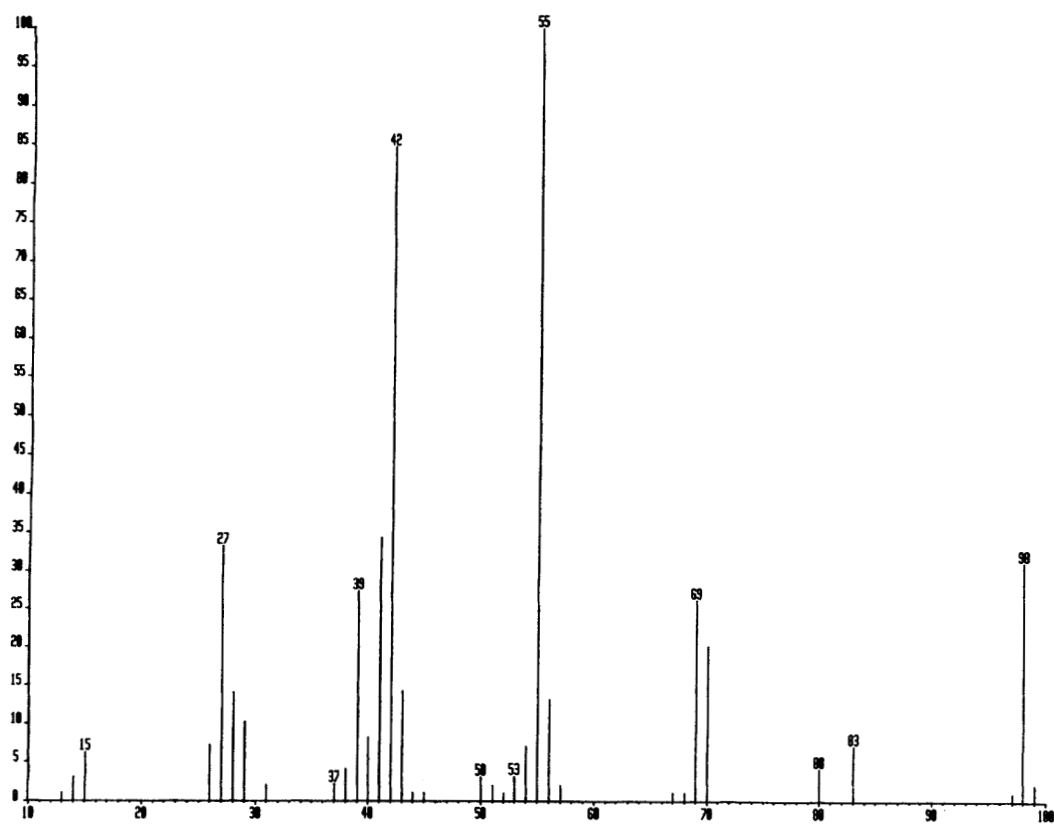


Sample 7.7

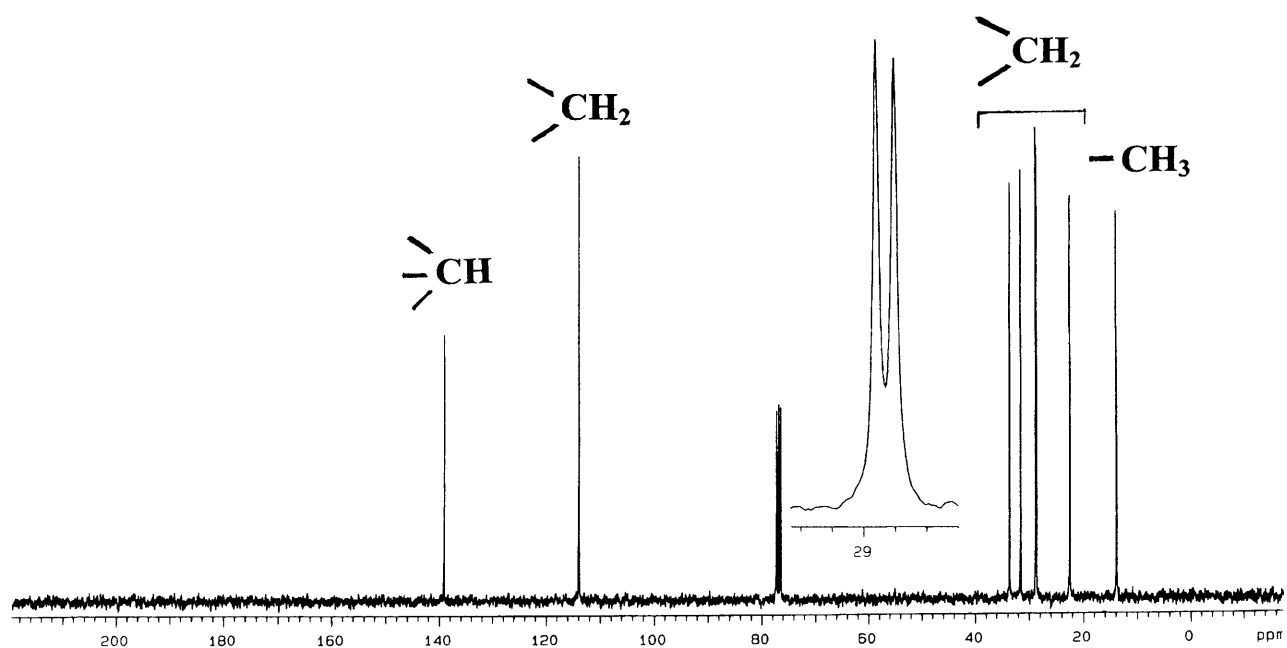
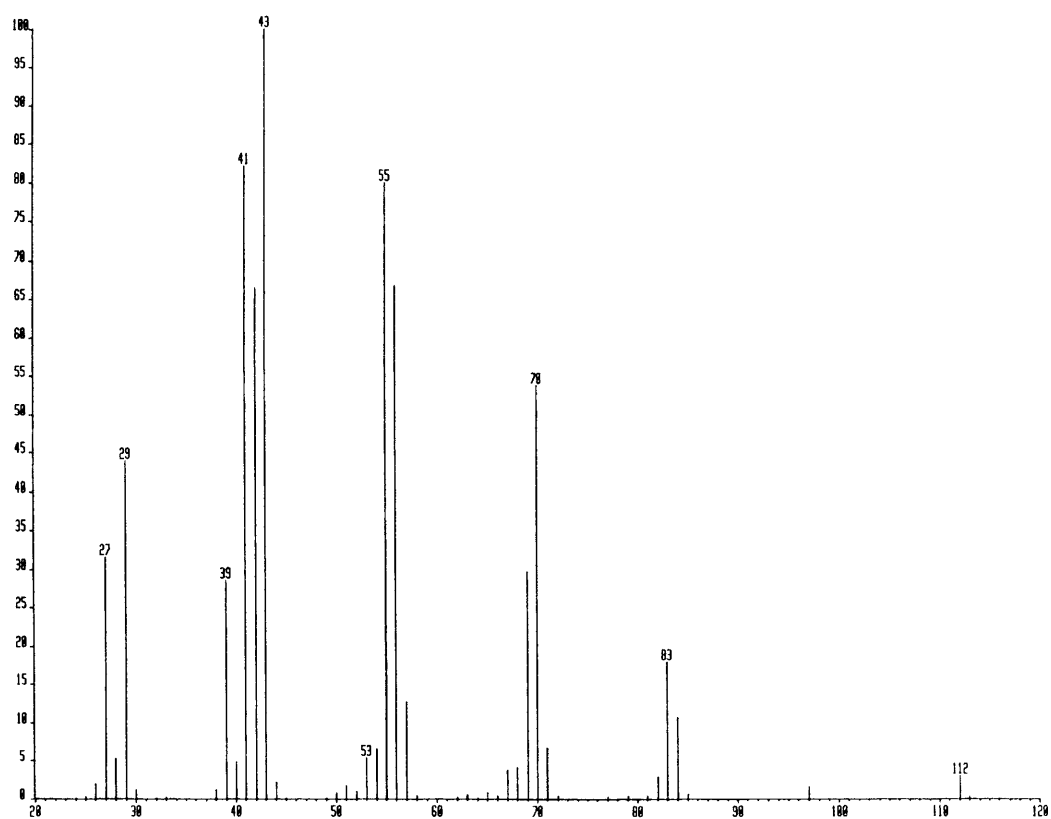




Sample 7.8



Sample 7.9



Sample 7.10



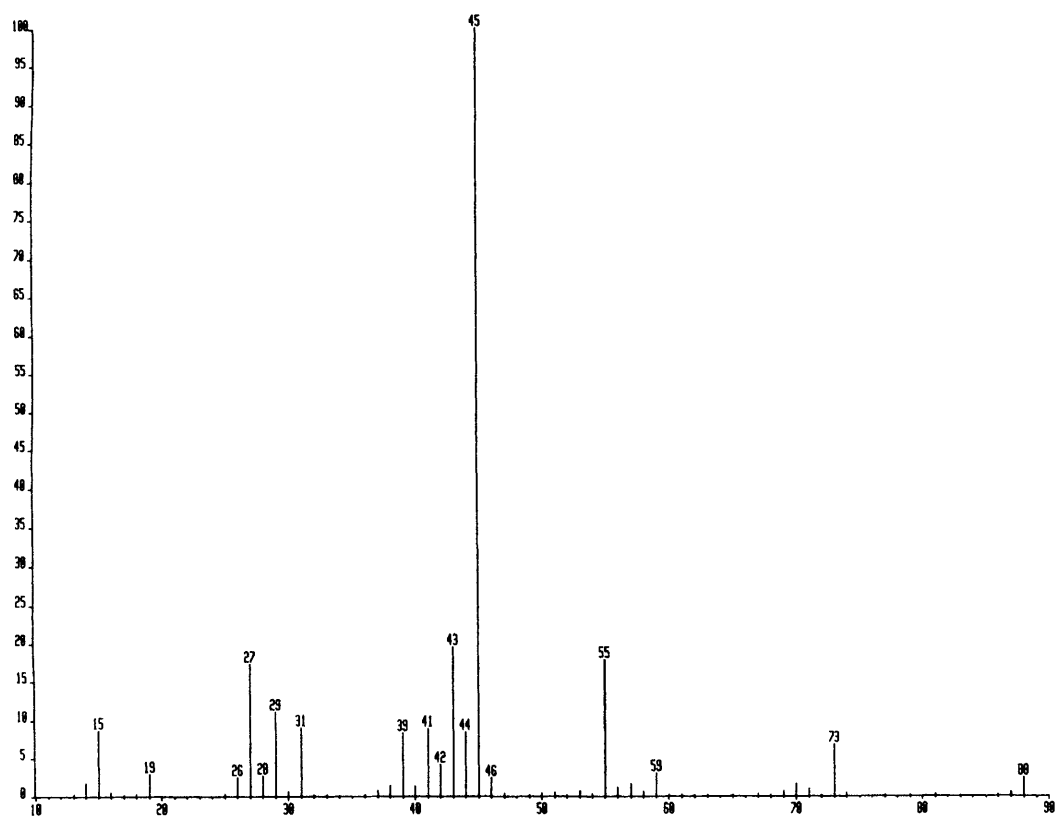
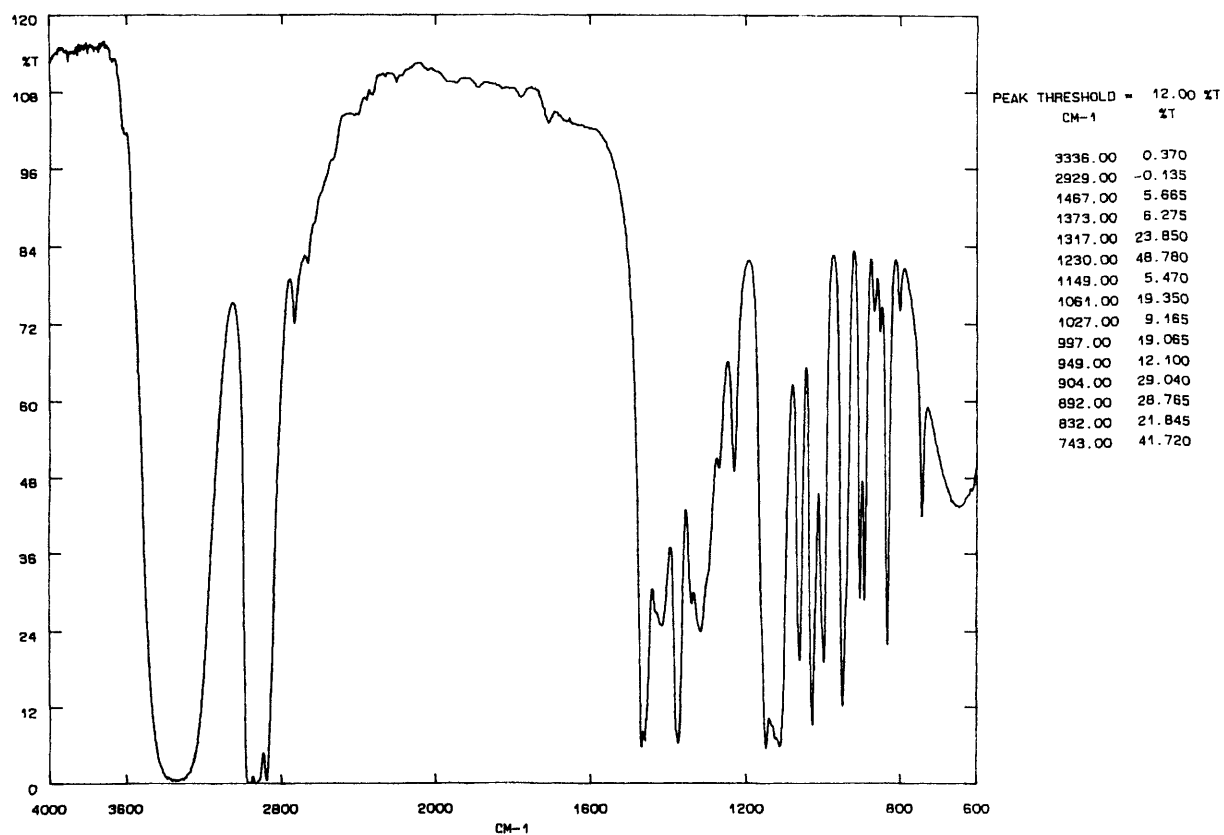
## **Problems in Interpreting Infrared Spectra, Mass Spectra, Ultraviolet Spectra and $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra**

We now combine four techniques, which enable us to get a full analysis of possible functional groups, give us the molecular weight and a lot of structural information about our samples. We are still restricted by branched chain compounds, and in some cases cannot distinguish between isomers, but these techniques do well on cyclic systems.

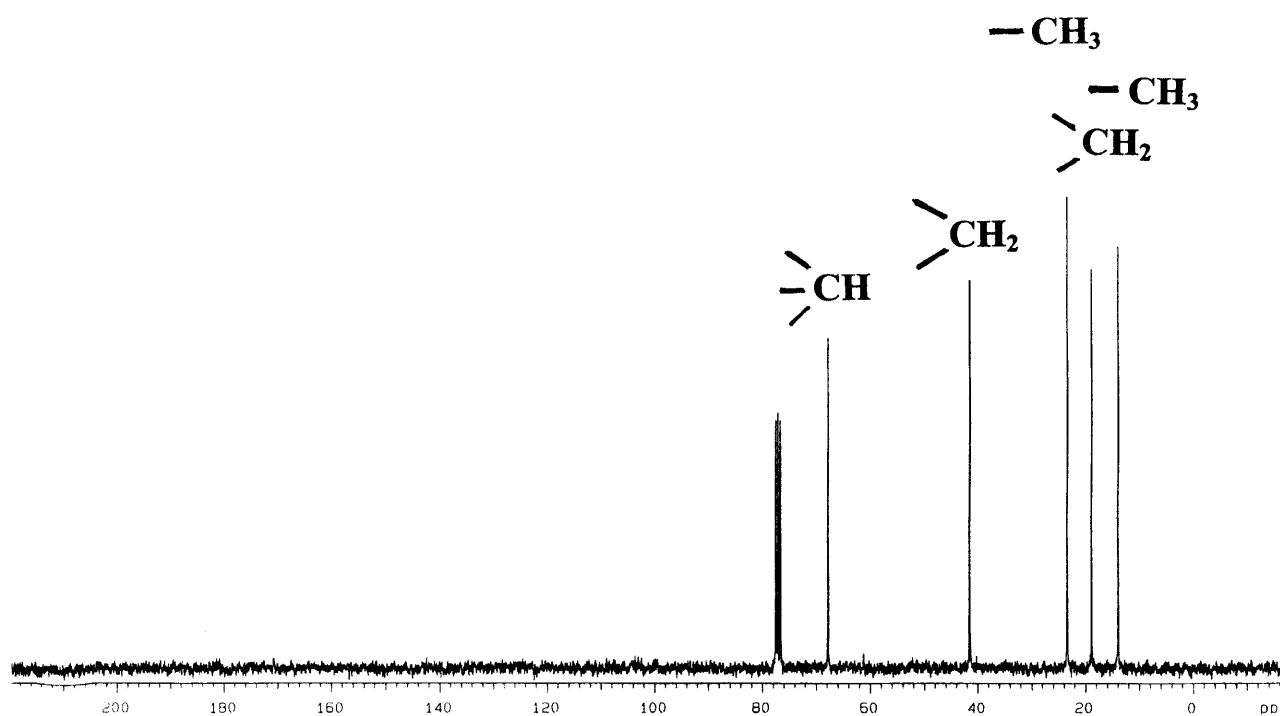
When combining these techniques it is usual to start with infrared, in order to identify the functional groups. Next, study the mass spectrum to obtain the molecular weight, halogen content and main splittings. The ultraviolet spectrum tells us about any conjugation. The  $^{13}\text{C}$  NMR spectrum should be checked to see if the C and H content and the functional groups add up to the molecular weight. If not, then the molecule has sufficient symmetry to place some atoms in identical environments.

Always remember, when you have assigned a structure, to check that your assignment is consistent with all the data from all the techniques.

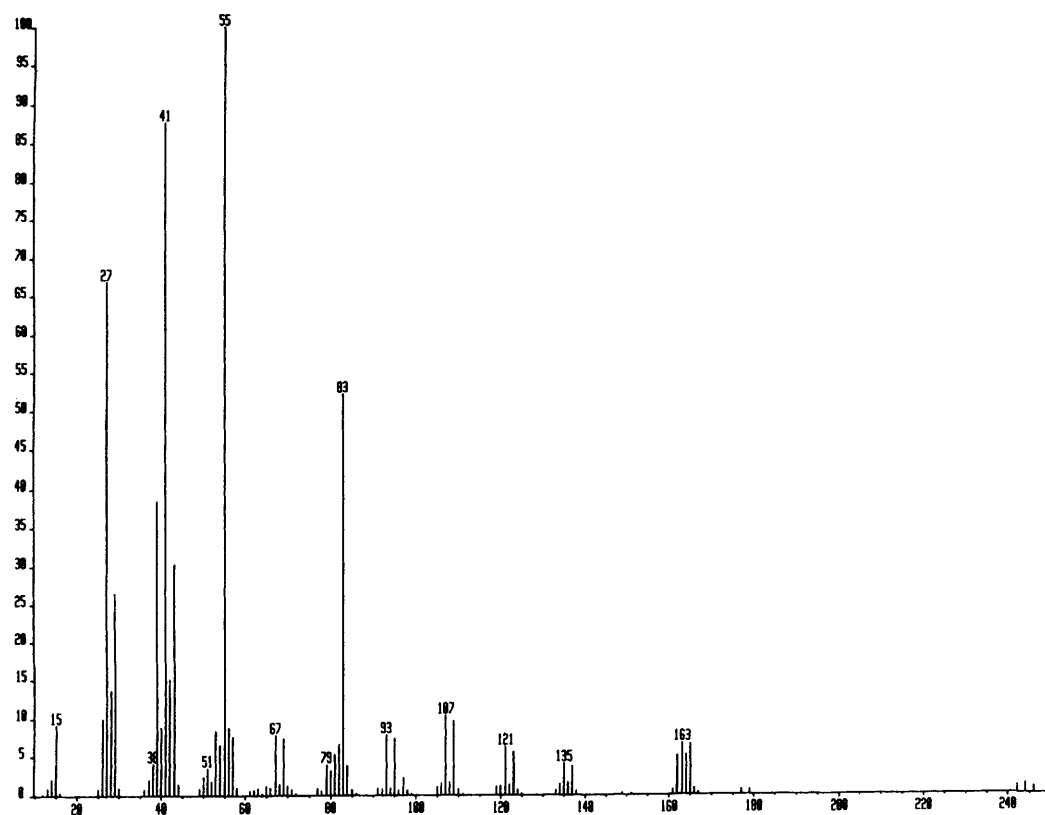
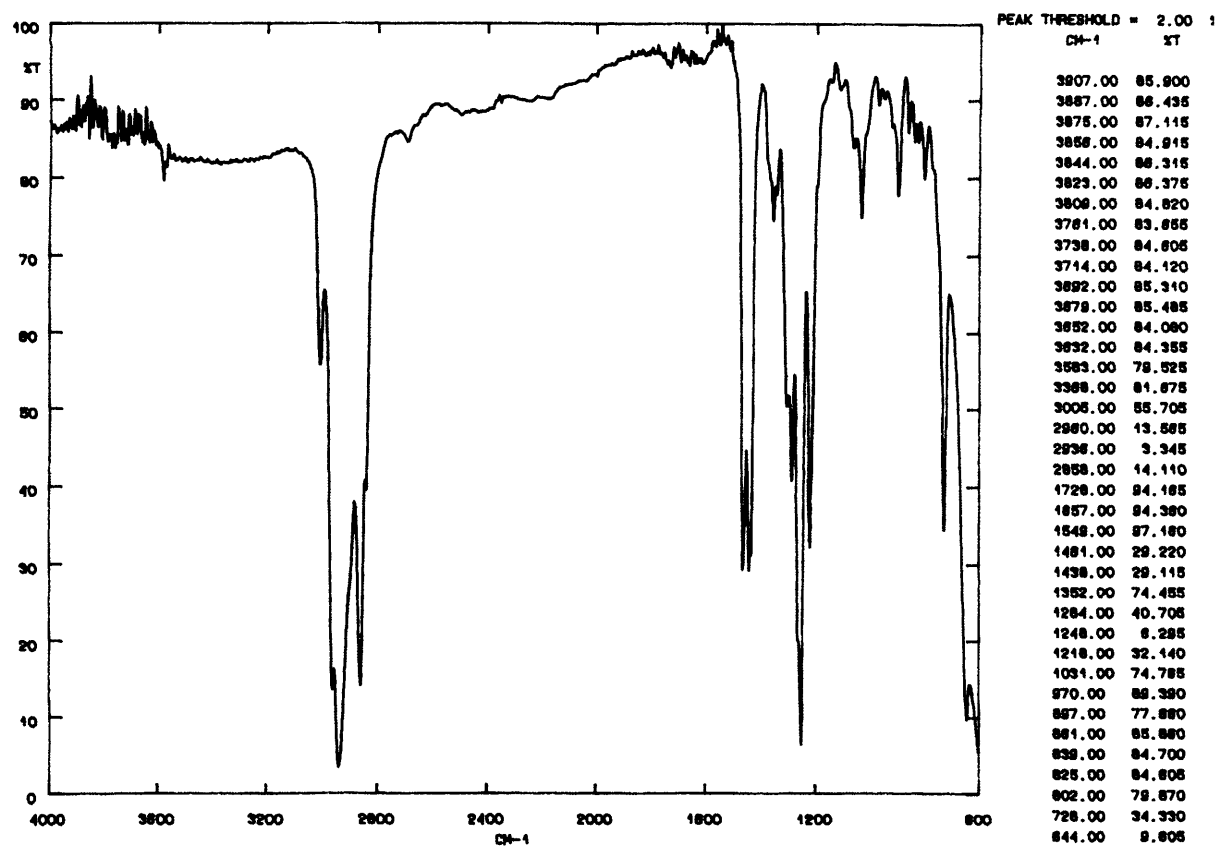
All the samples in the exercise can be identified using the data provided.



Sample 8.1

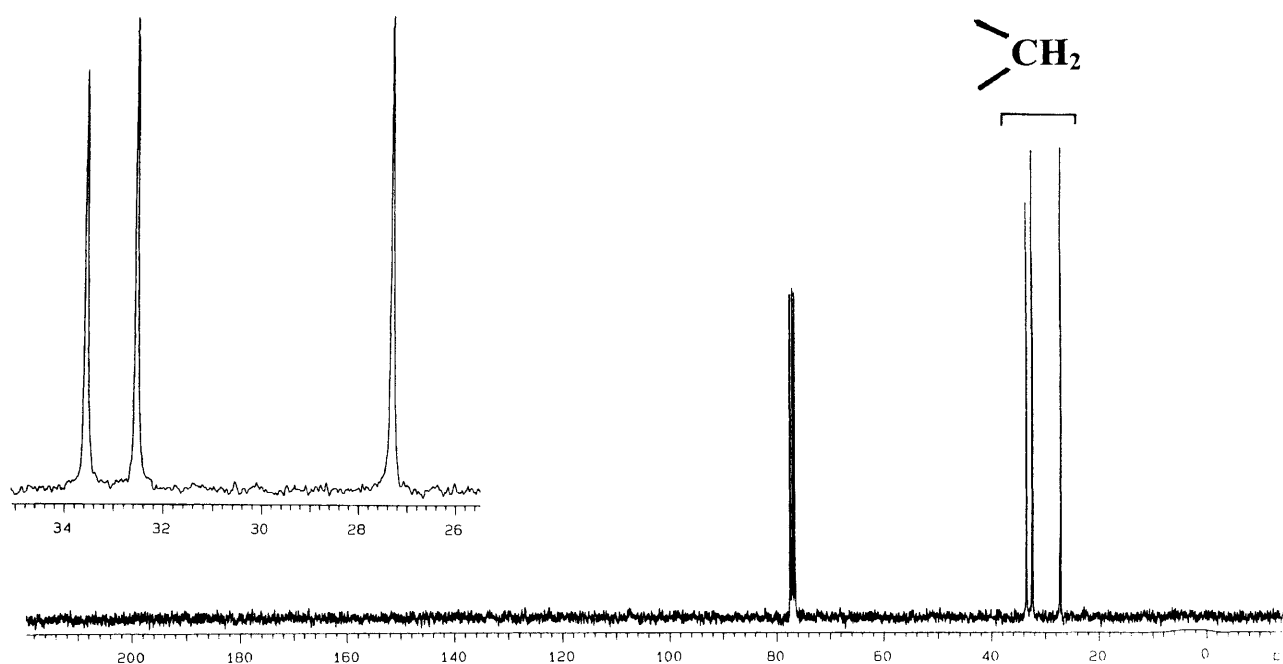


Sample 8.1 Continued

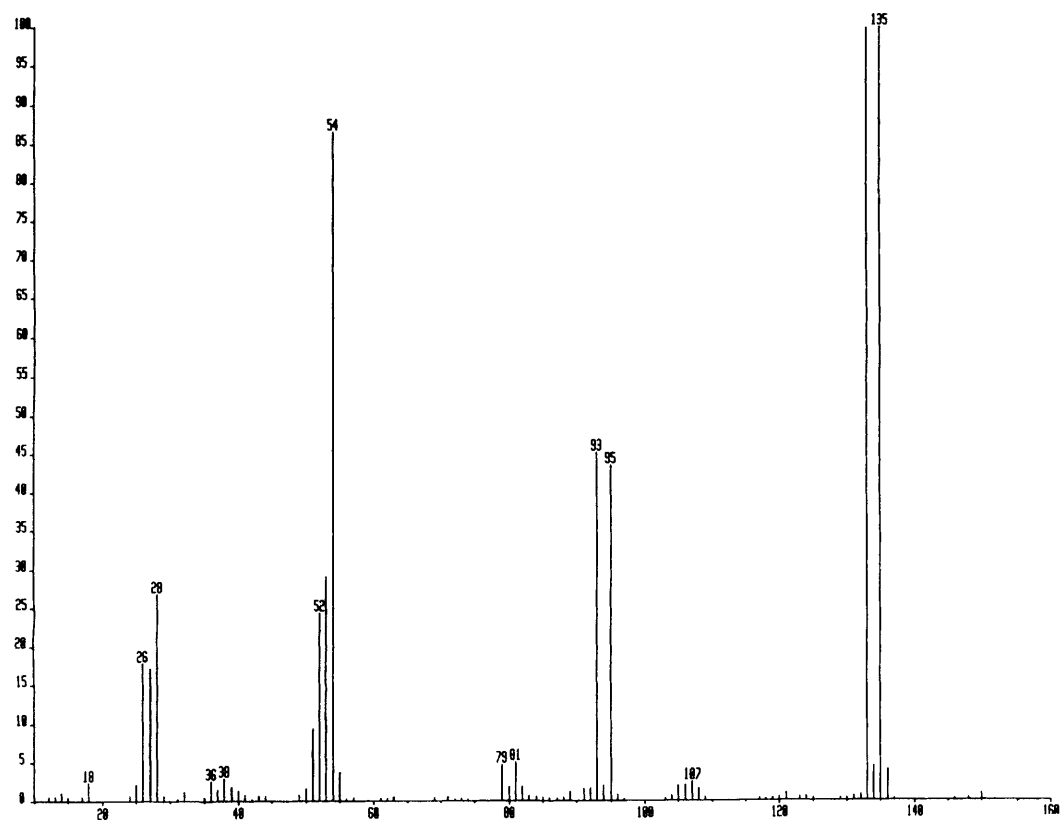
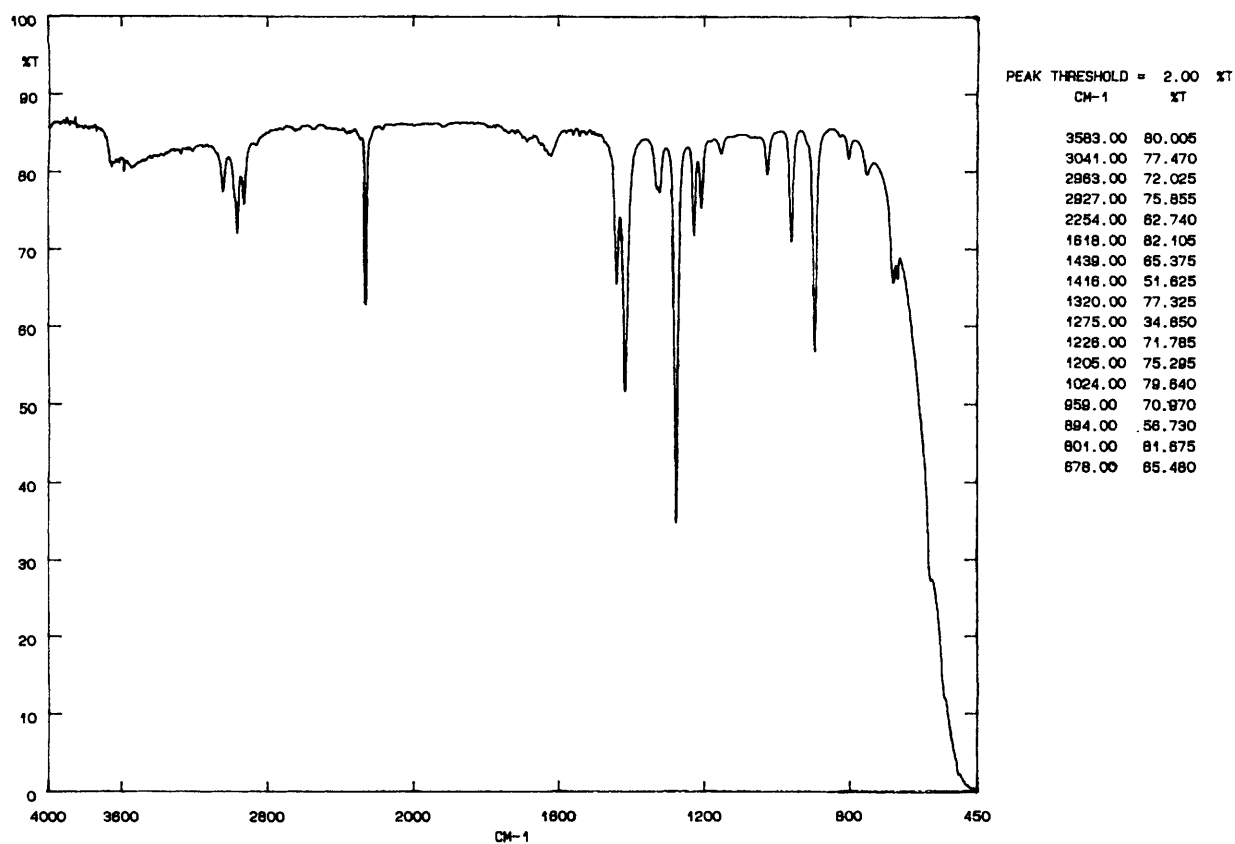


Sample 8.2

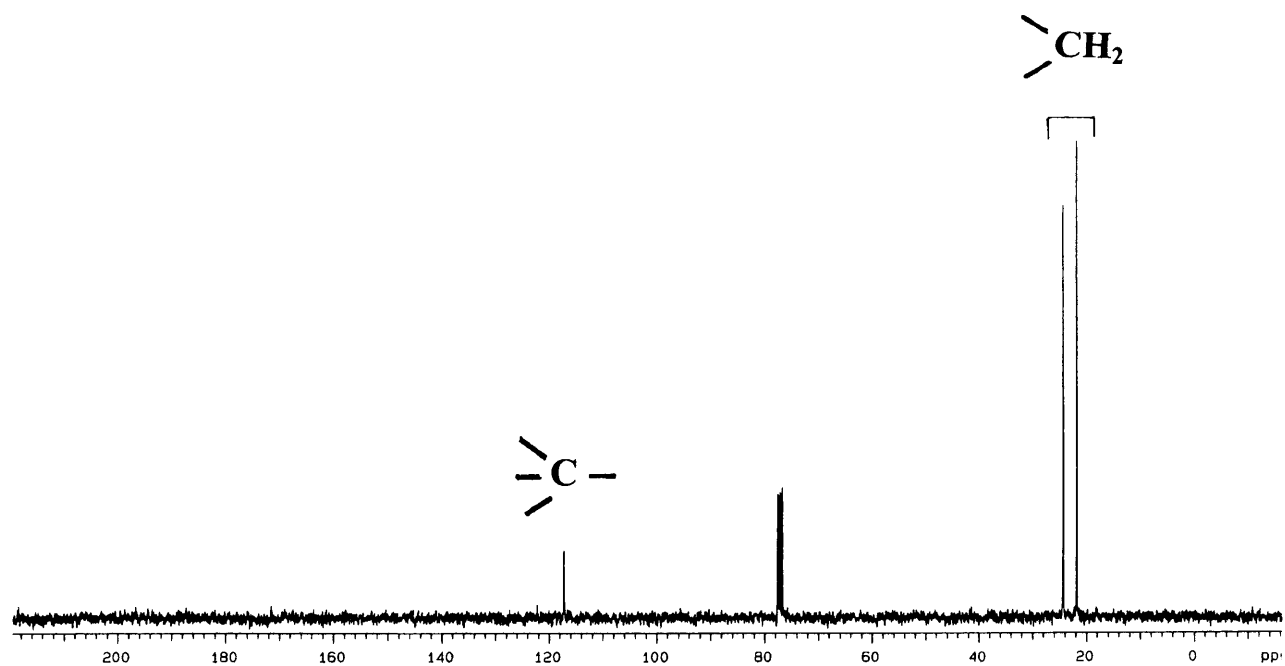




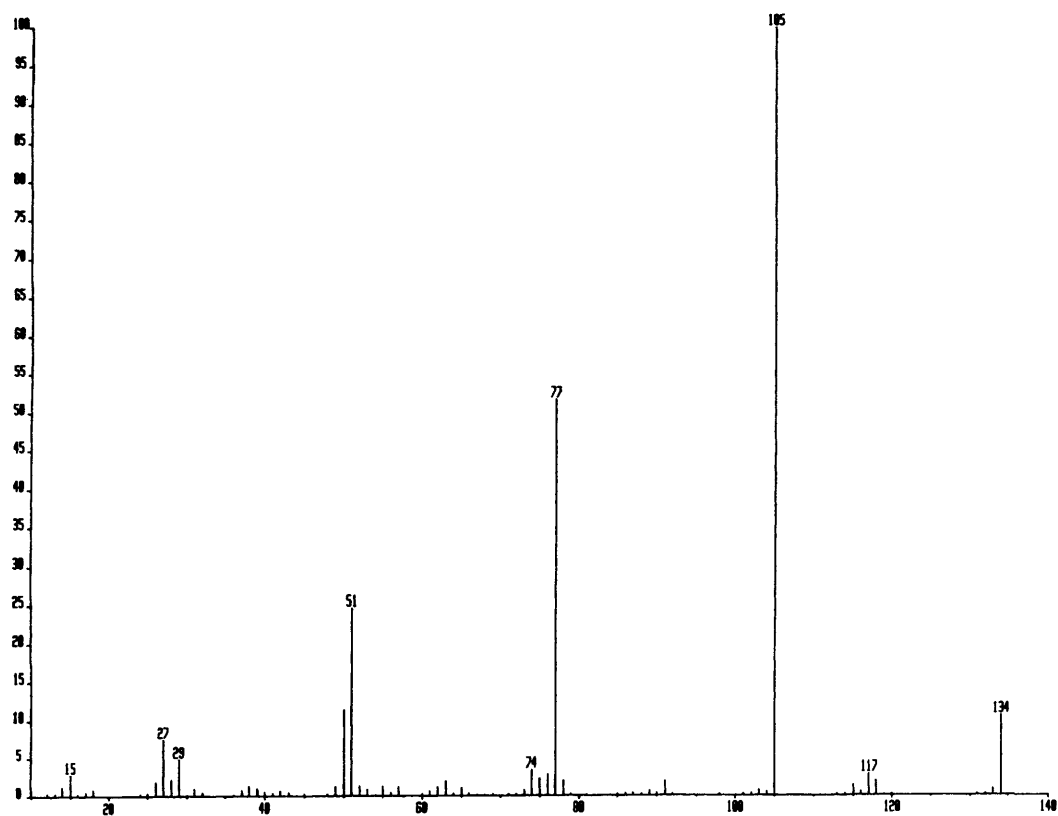
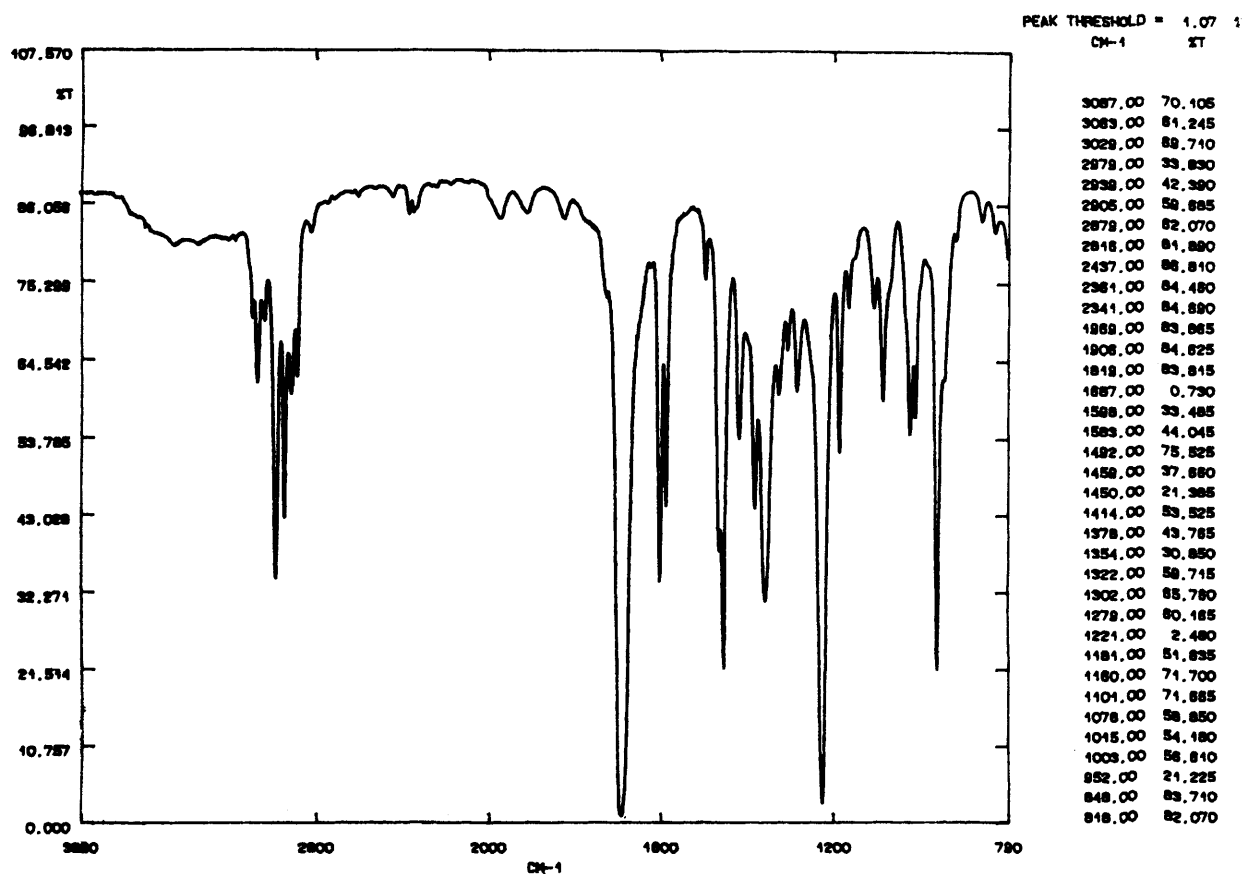
Sample 8.2 Continued



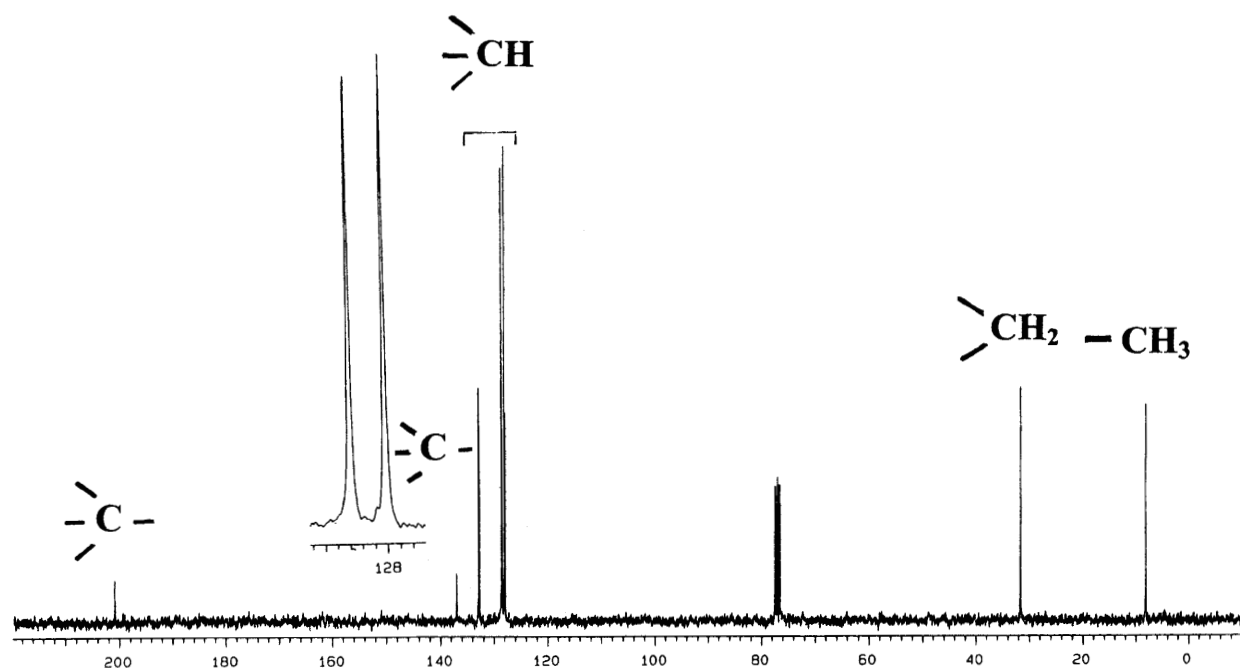
Sample 8.3



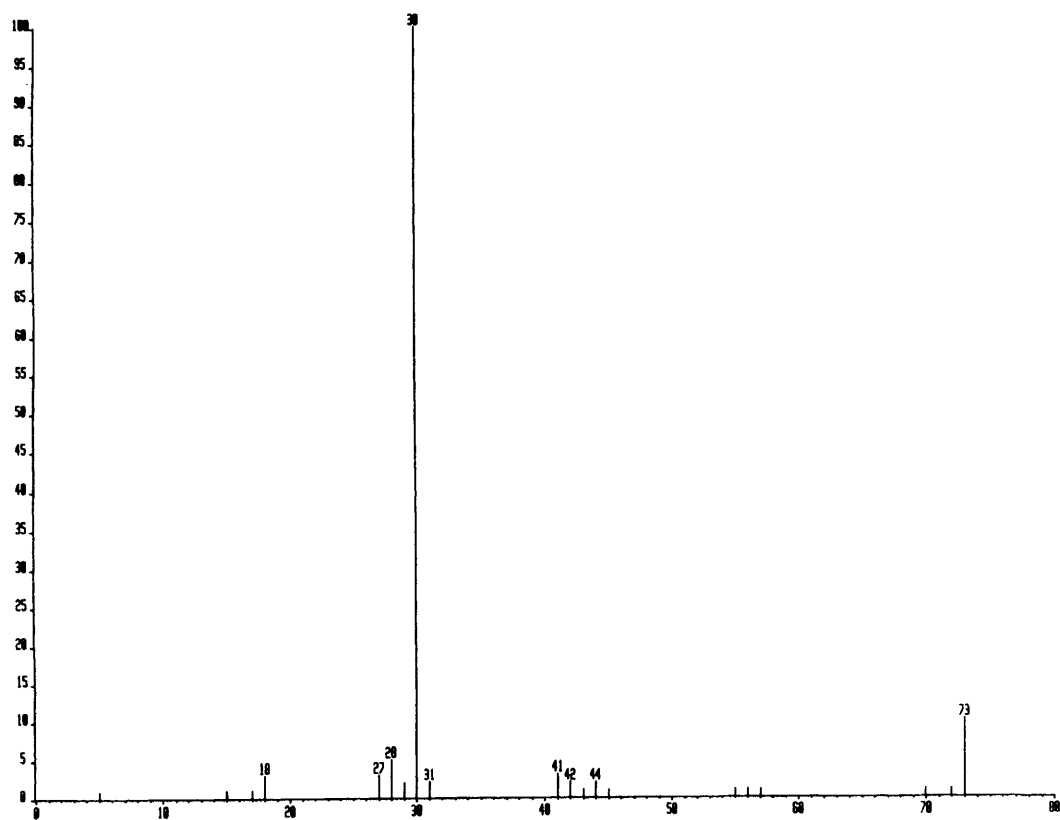
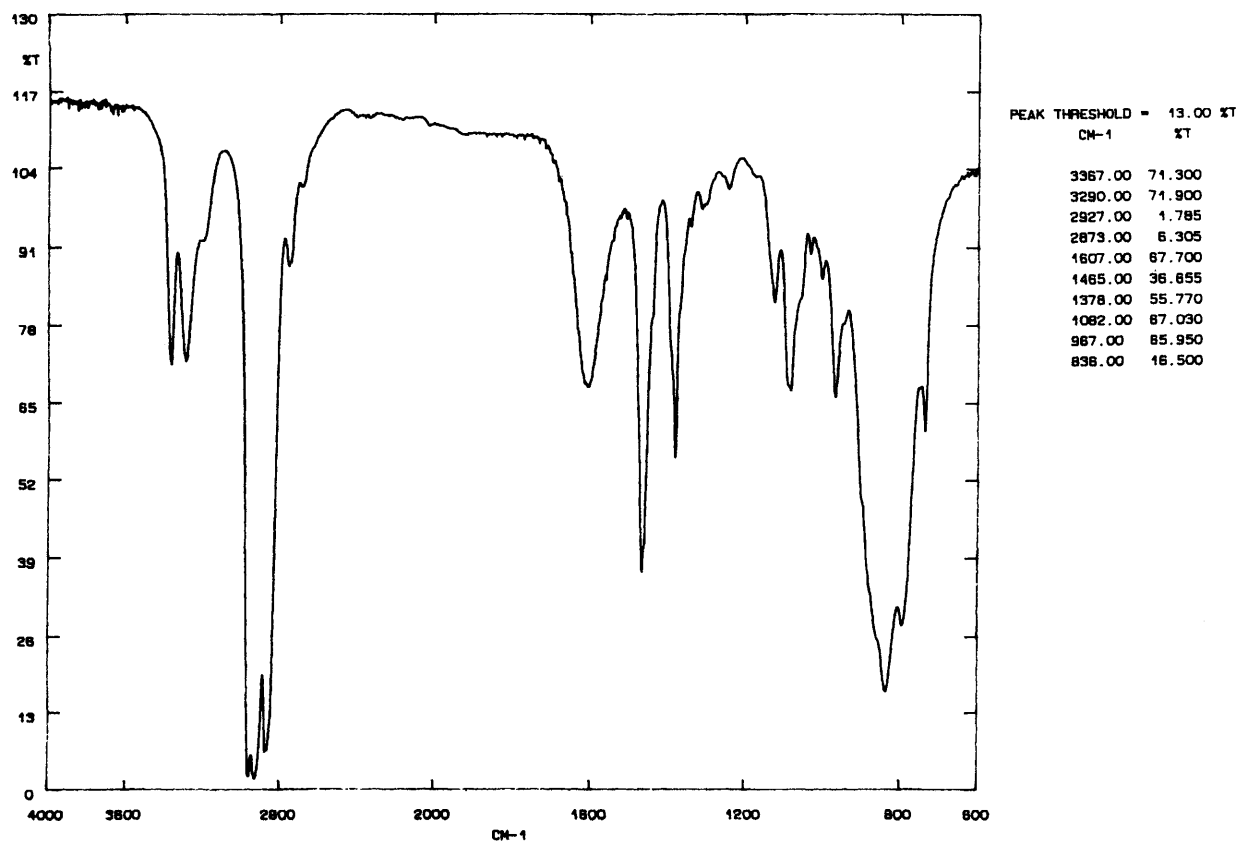
Sample 8.3 Continued



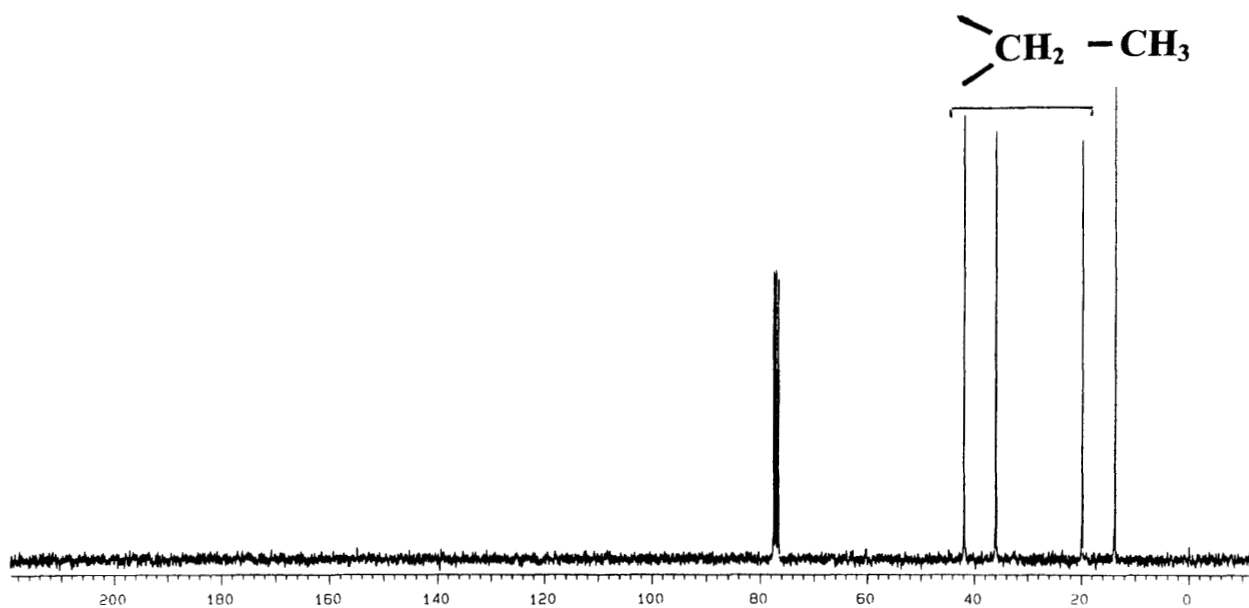
Sample 8.4



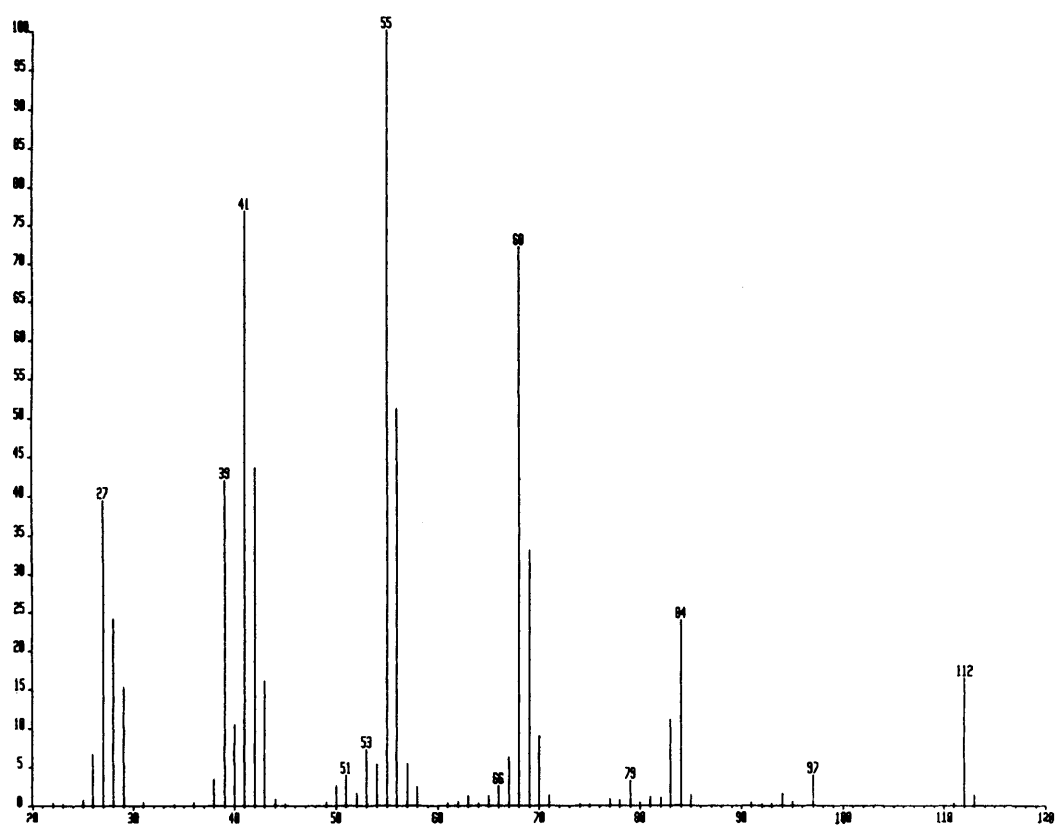
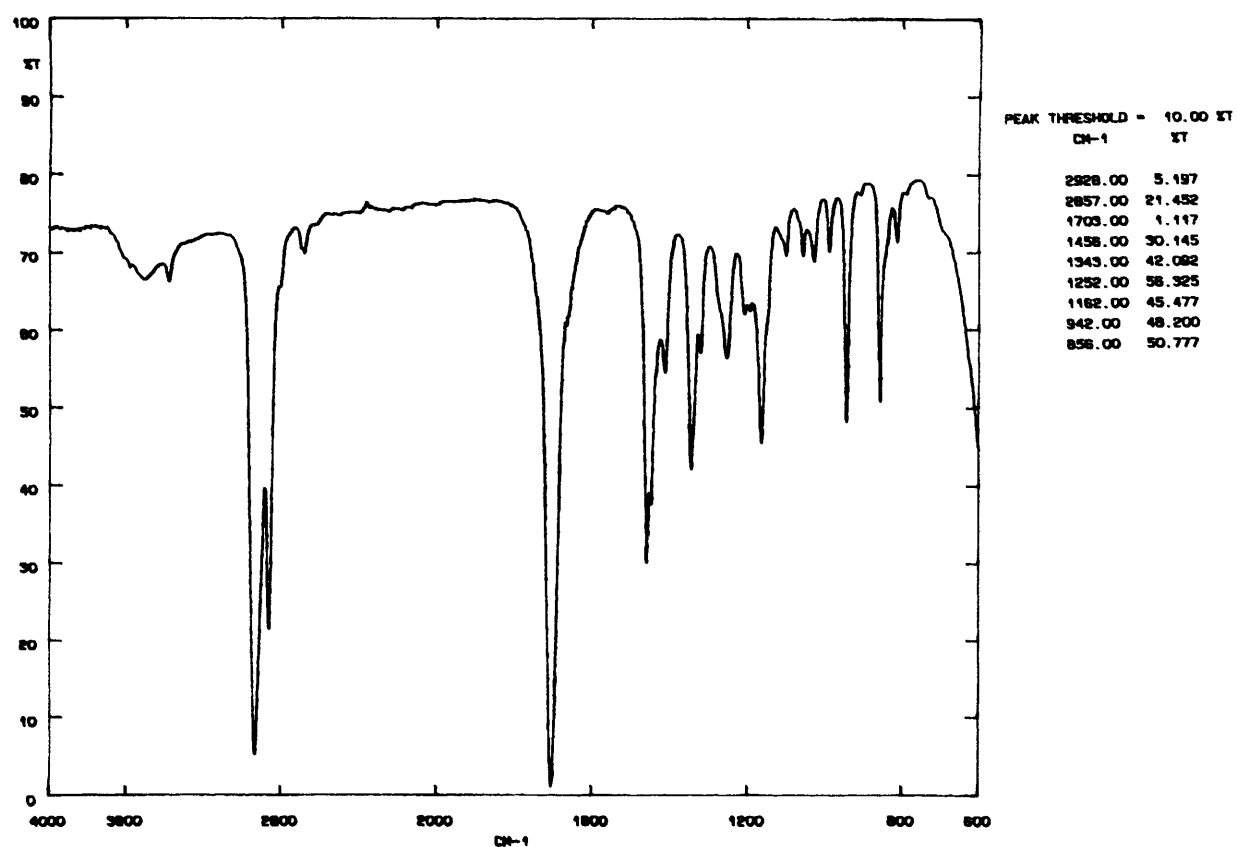
Sample 8.4 Continued



Sample 8.5

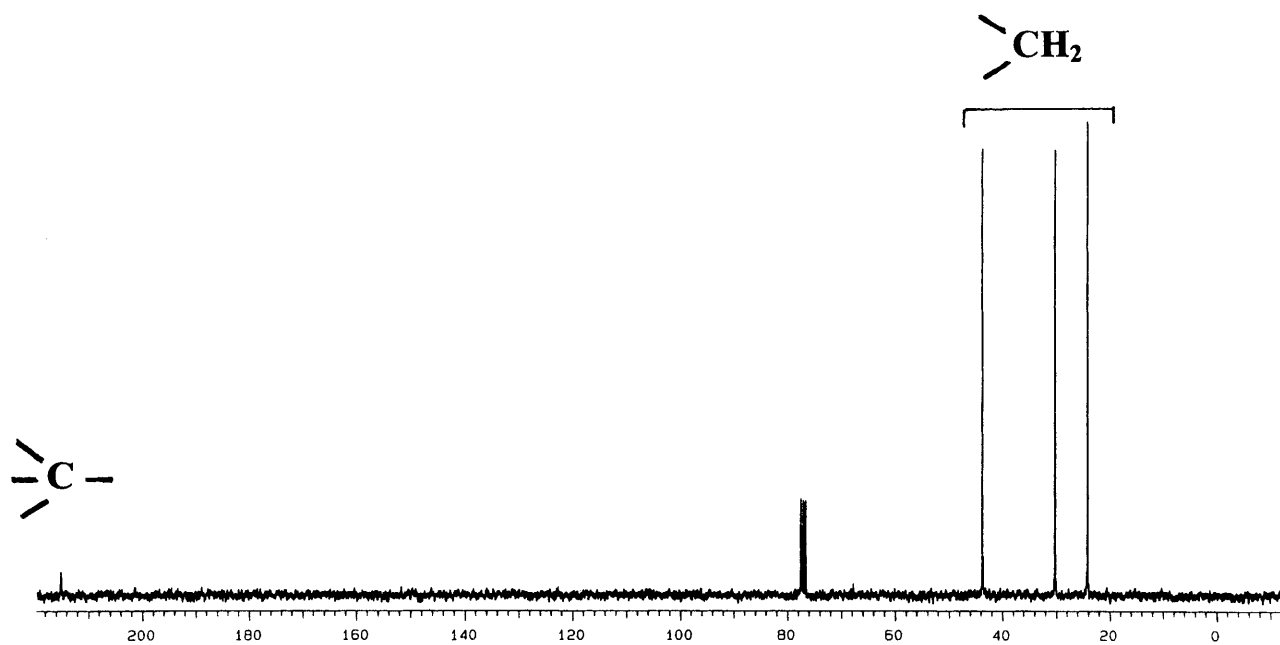


Sample 8.5 Continued

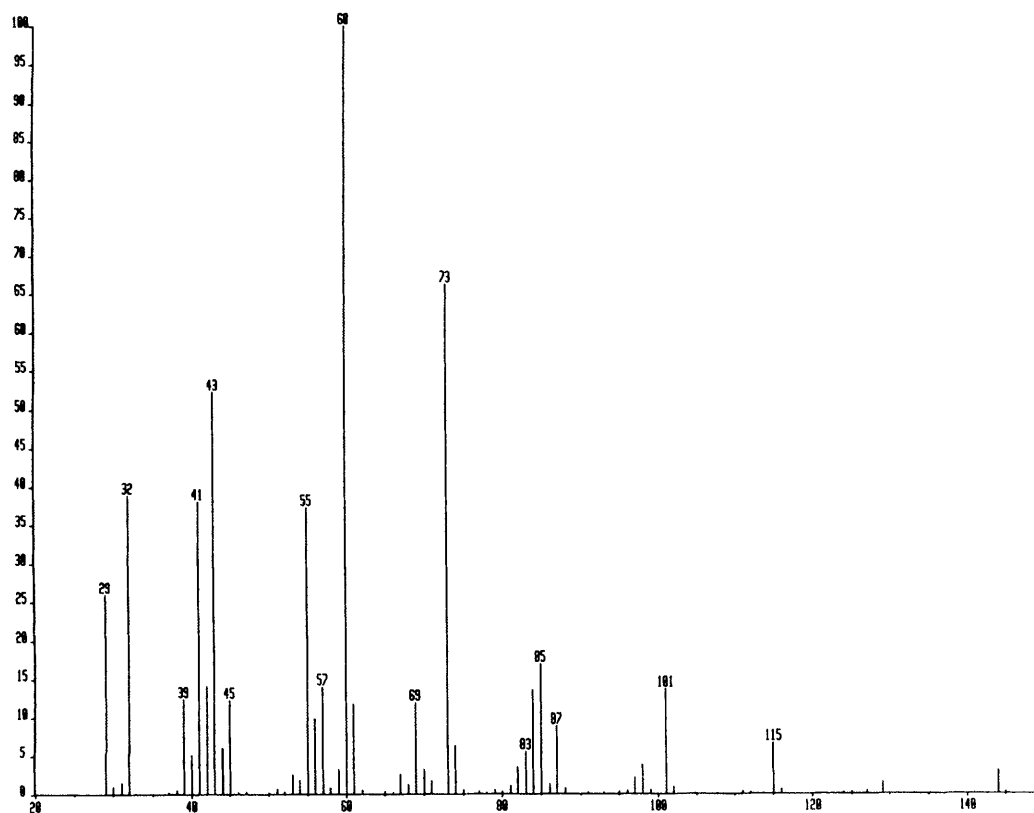
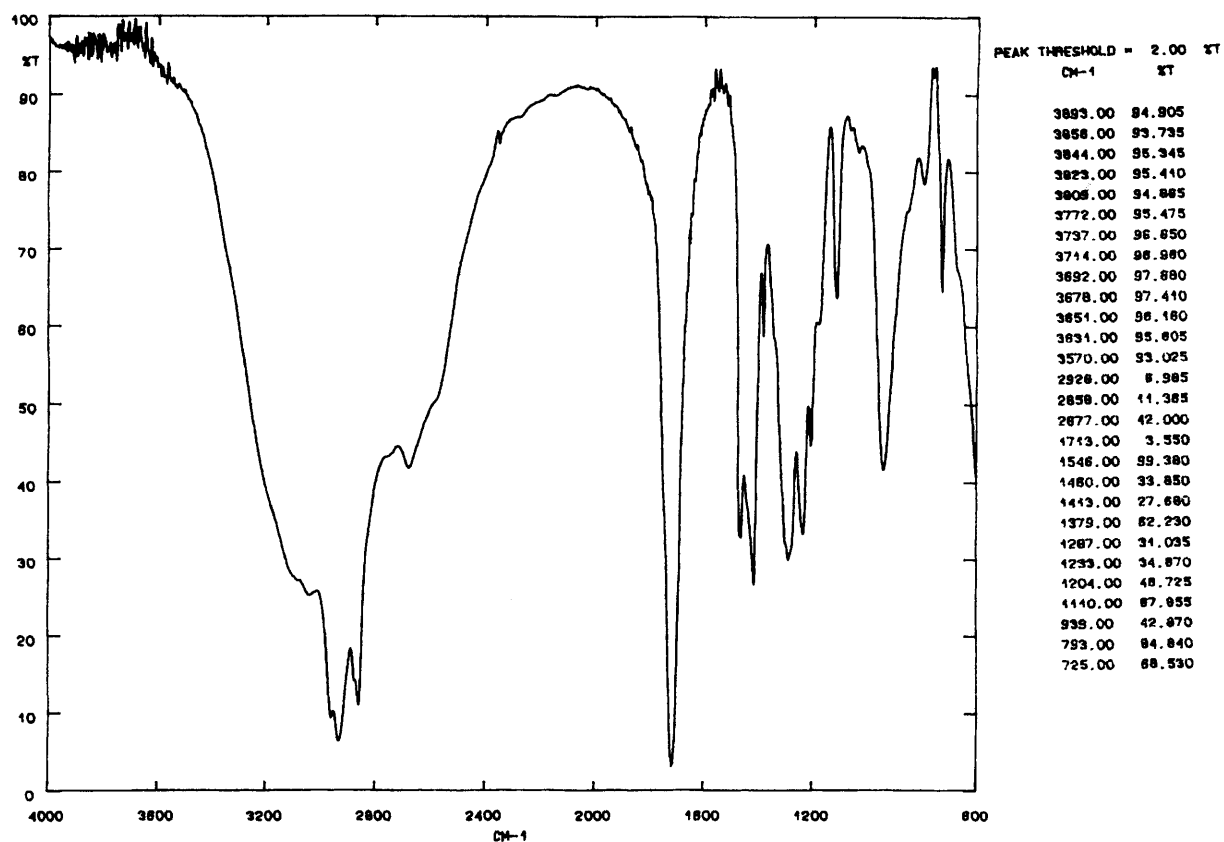


Sample 8.6

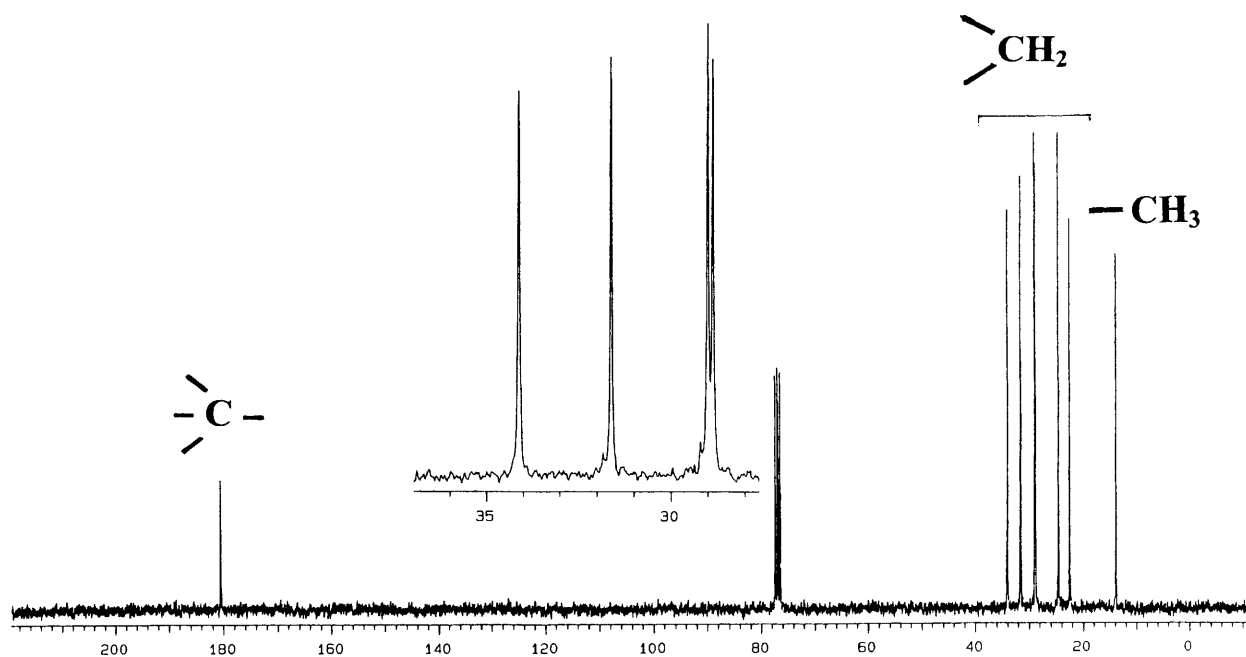




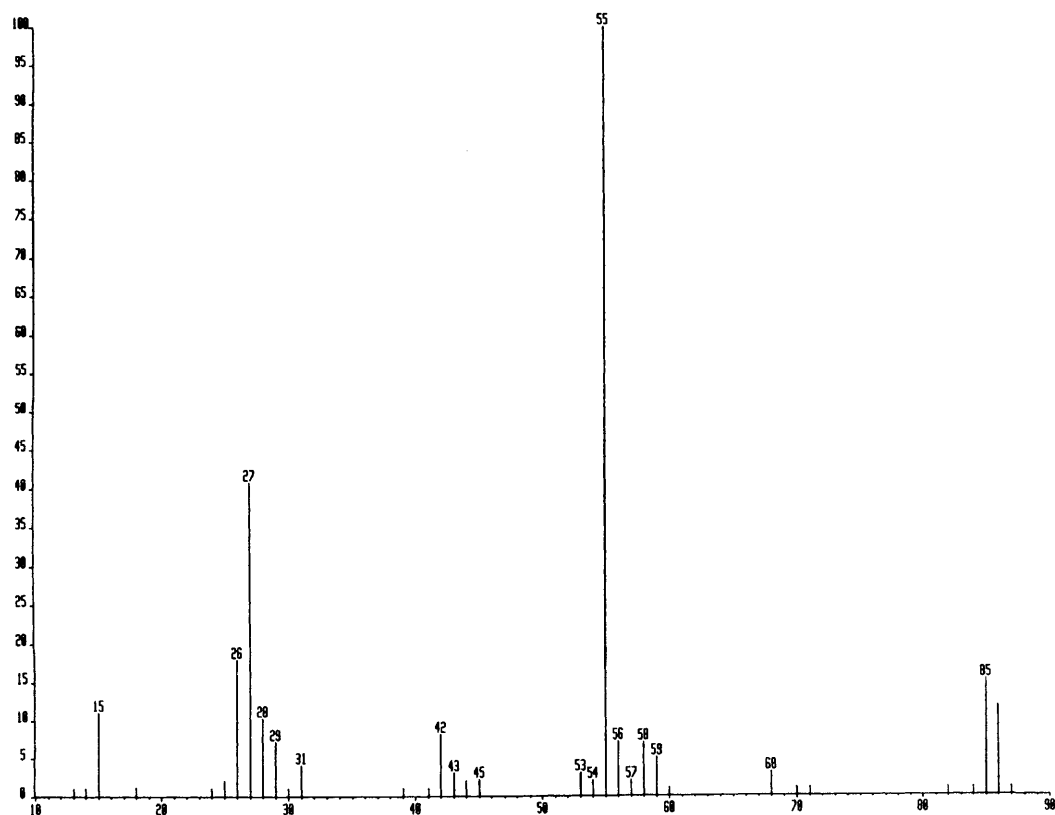
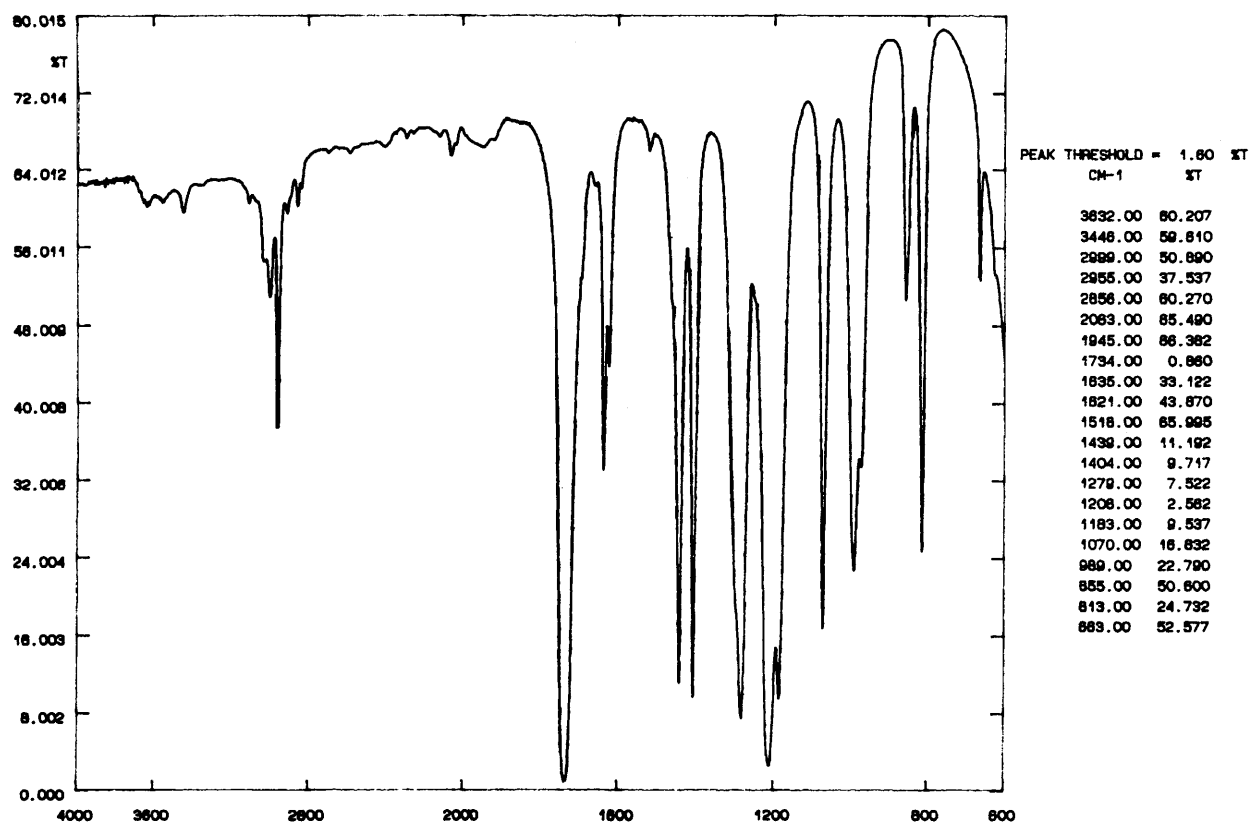
Sample 8.6 Continued



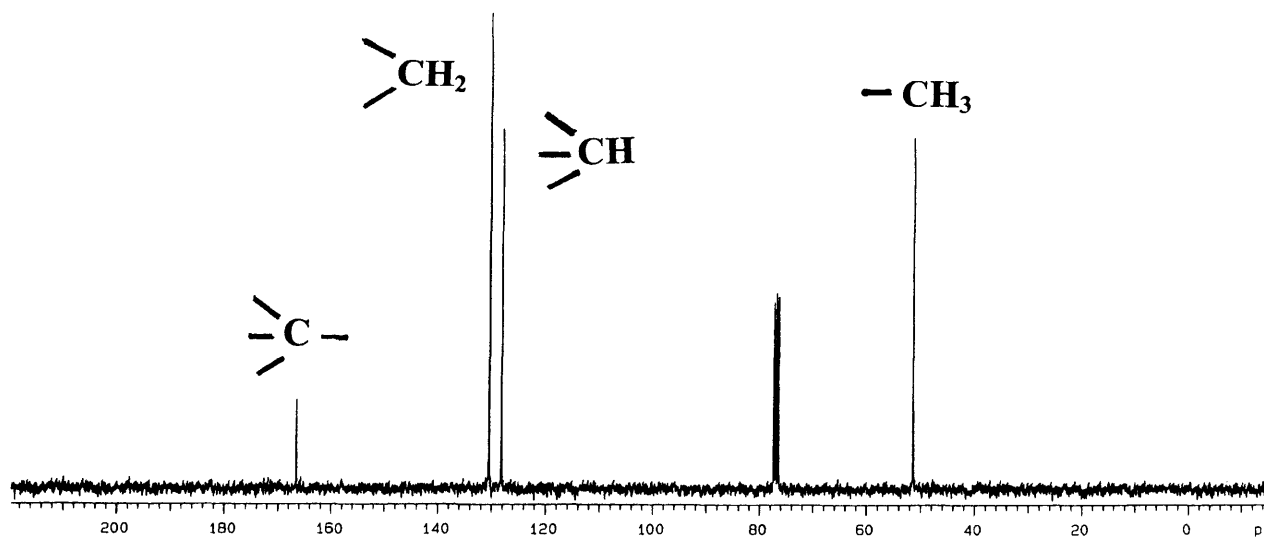
Sample 8.7



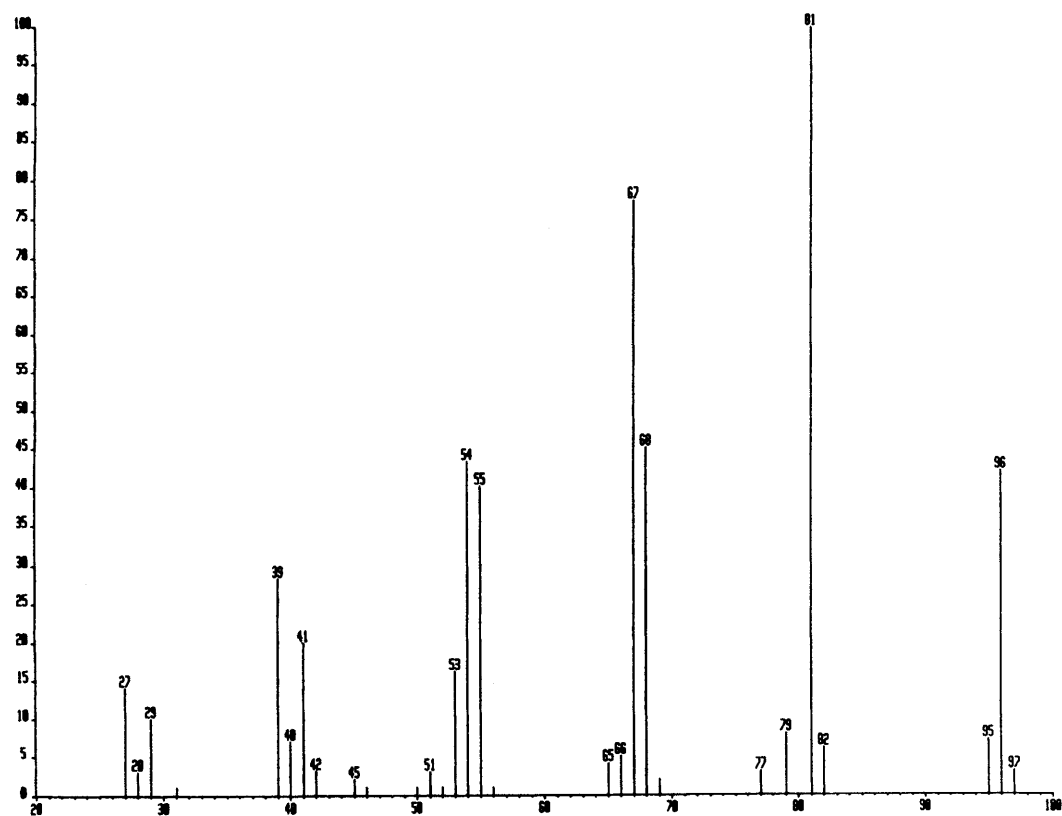
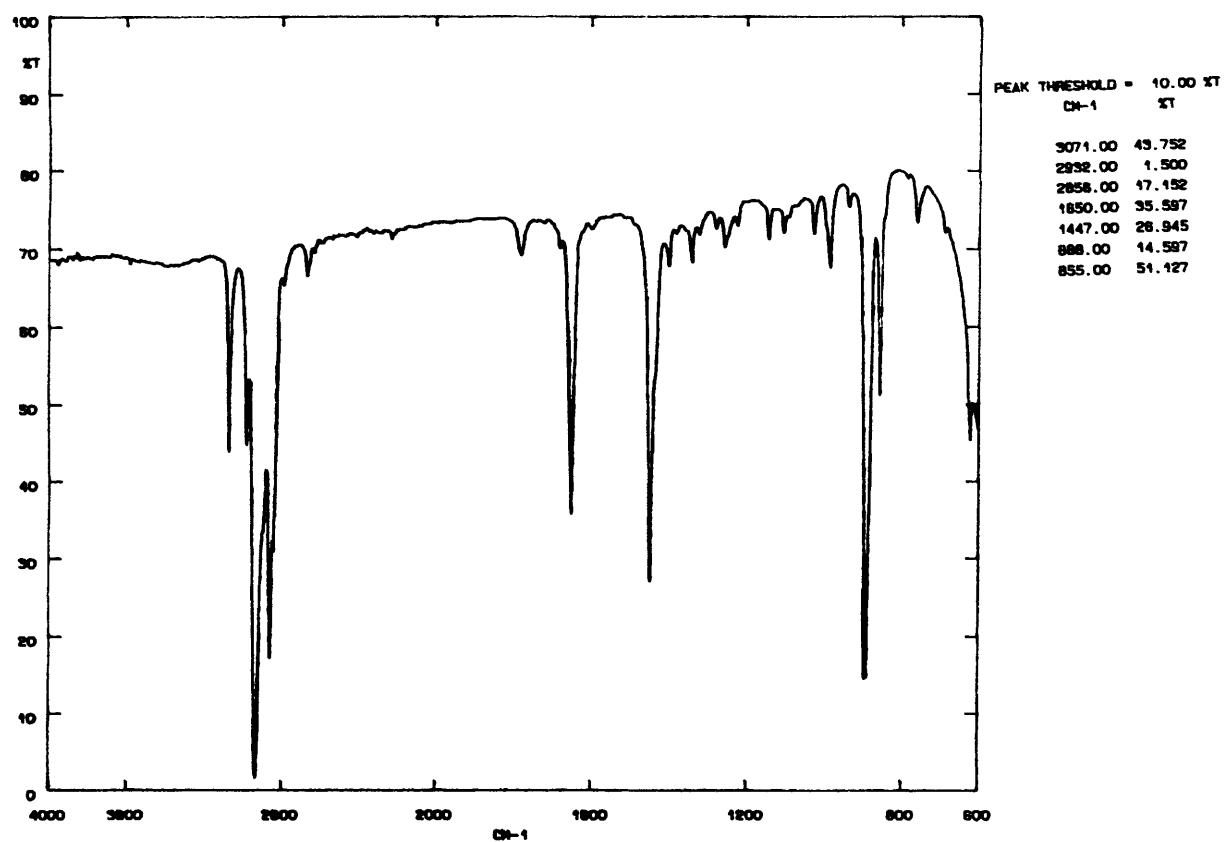
Sample 8.7 Continued



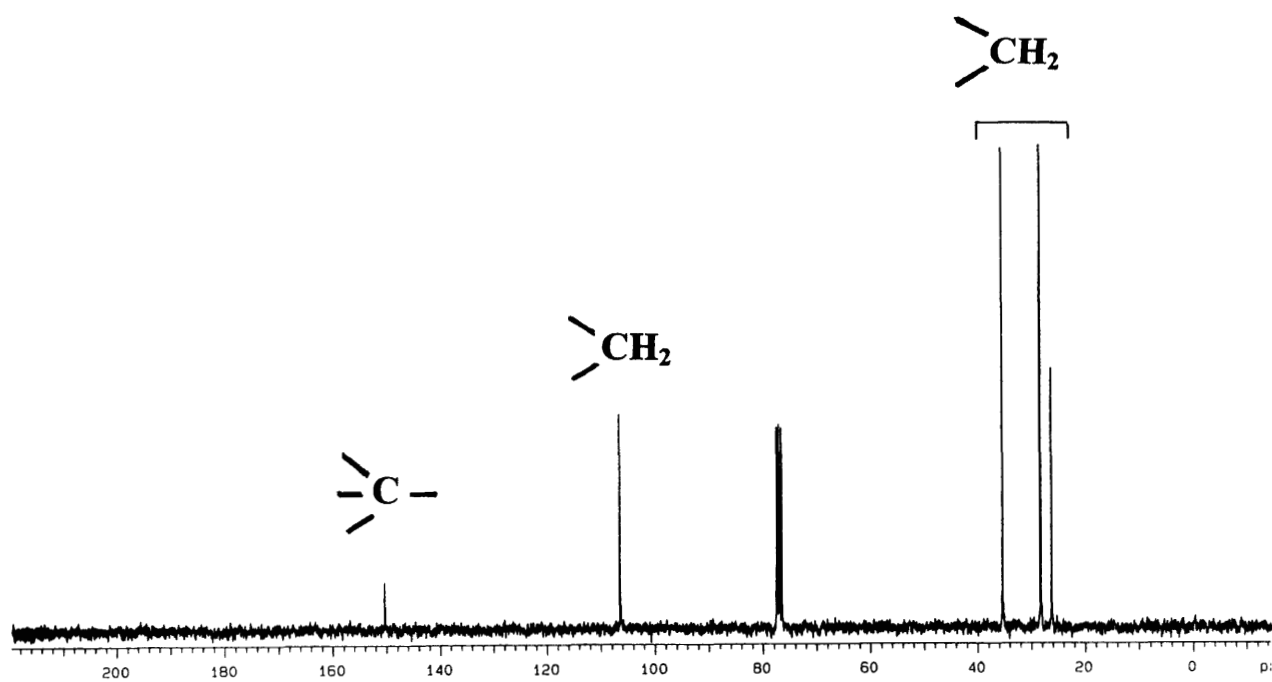
Sample 8.8



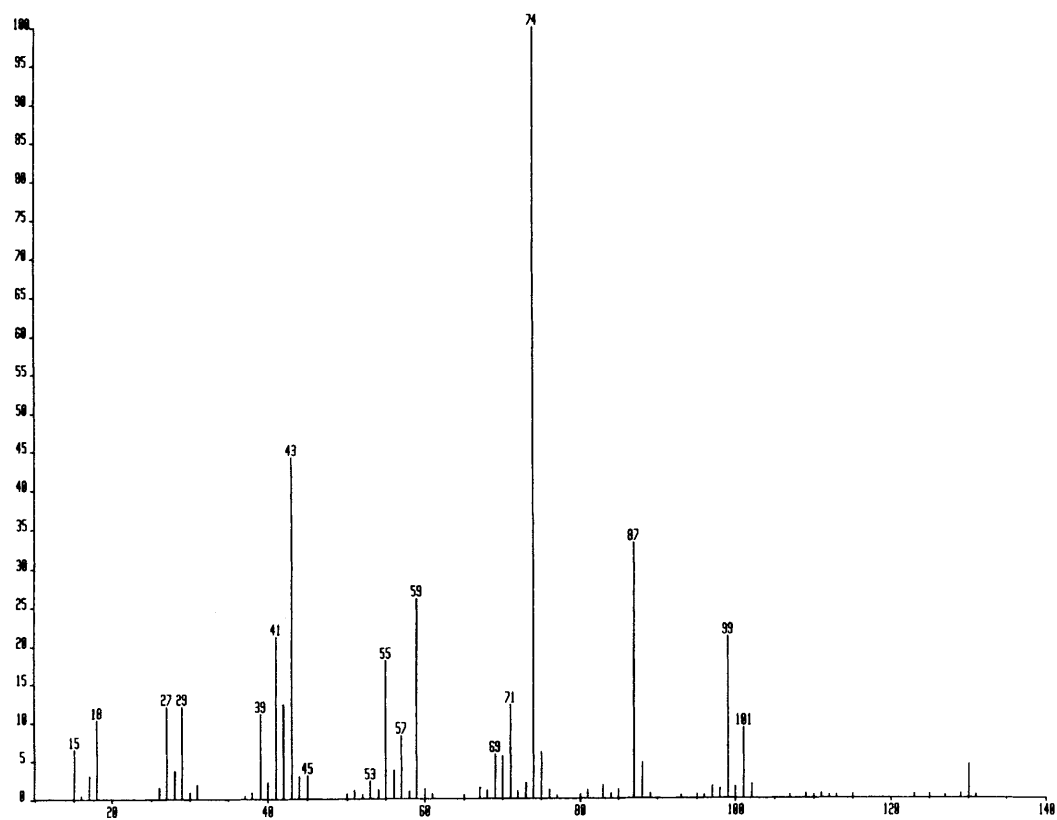
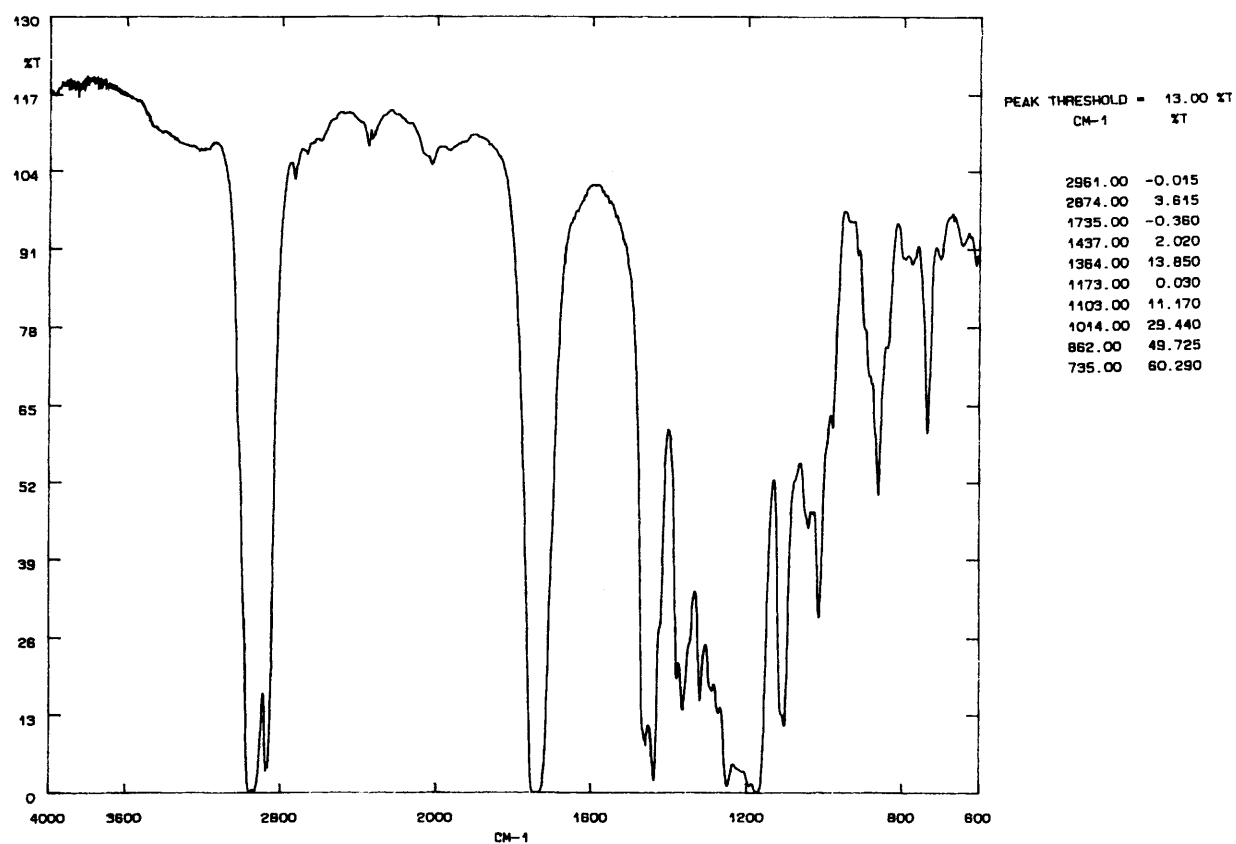
Sample 8.8 Continued



Sample 8.9

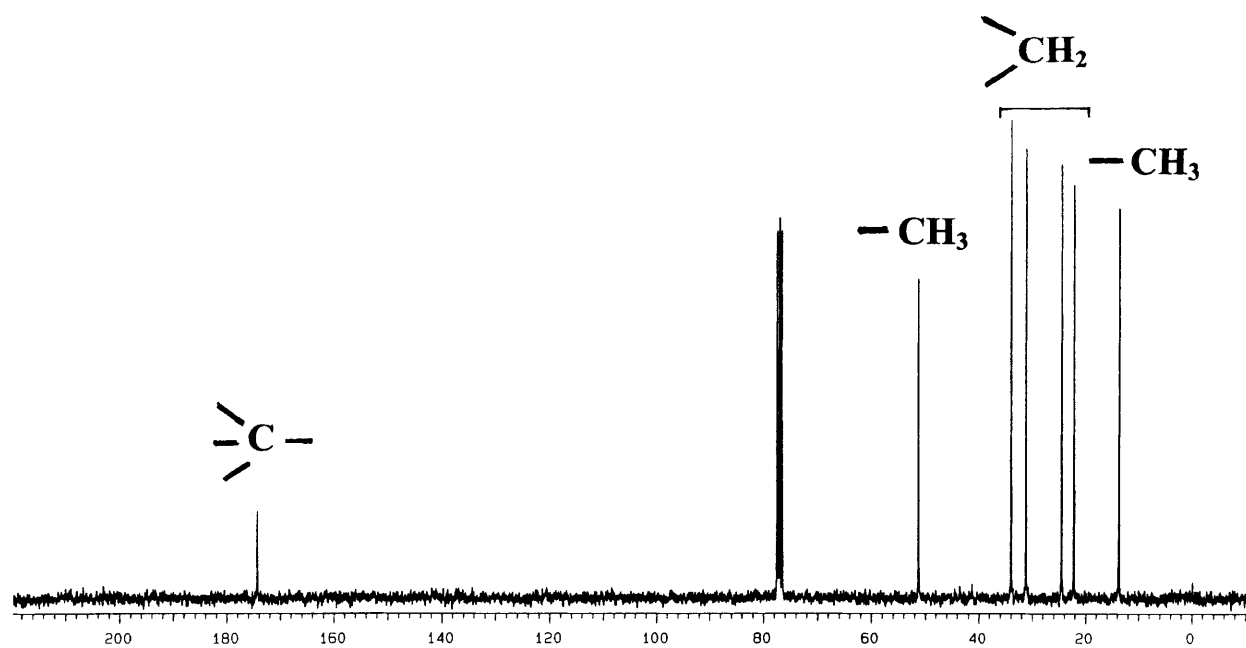


Sample 8.9 Continued

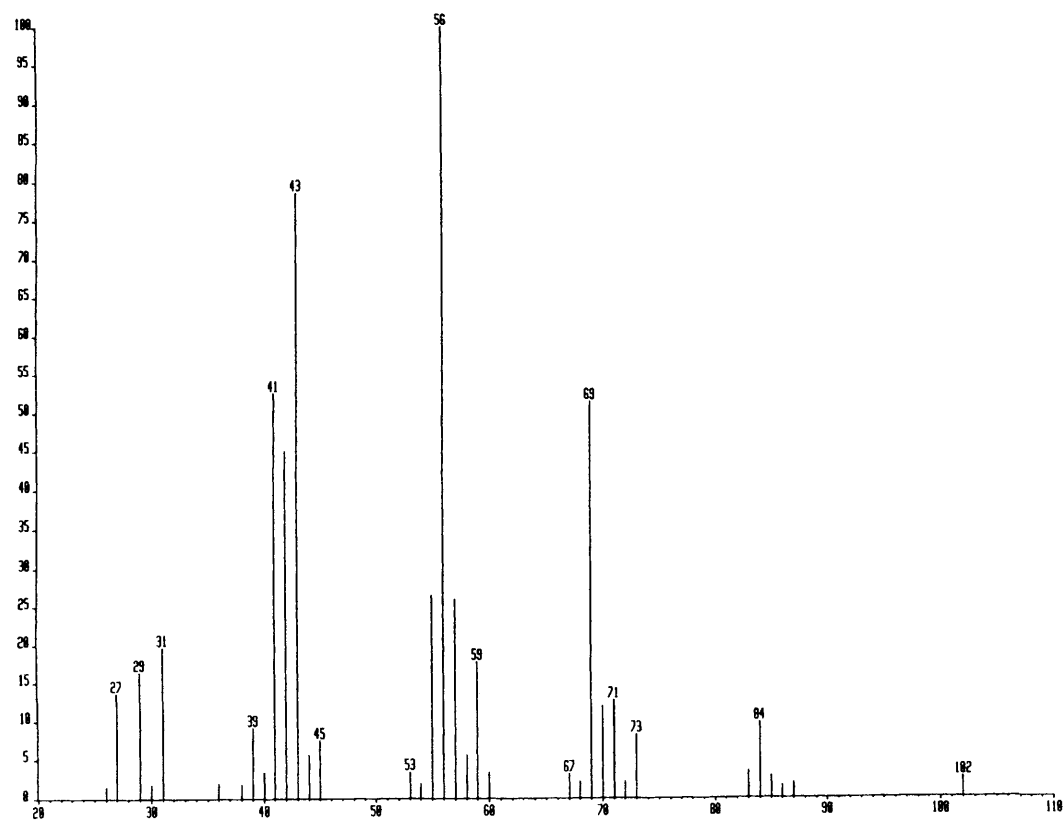
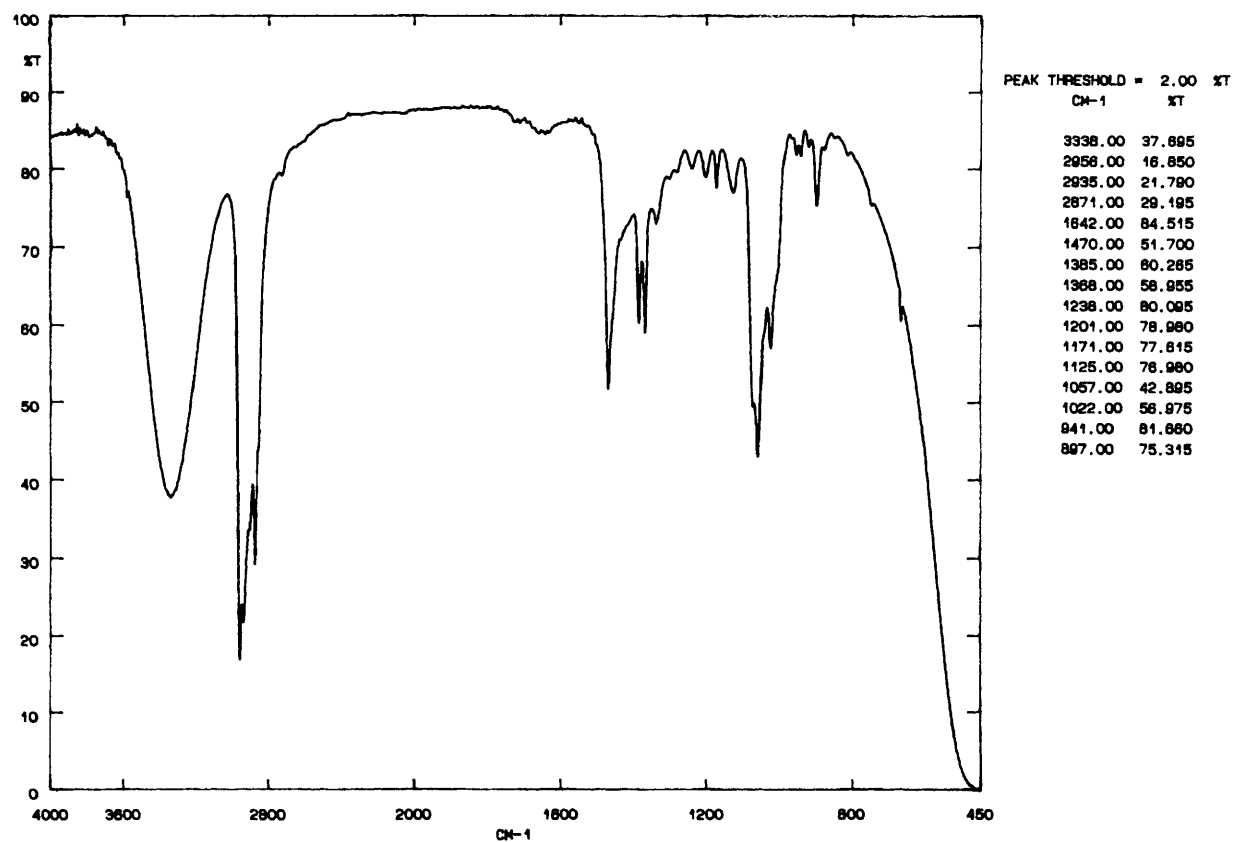


Sample 8.10

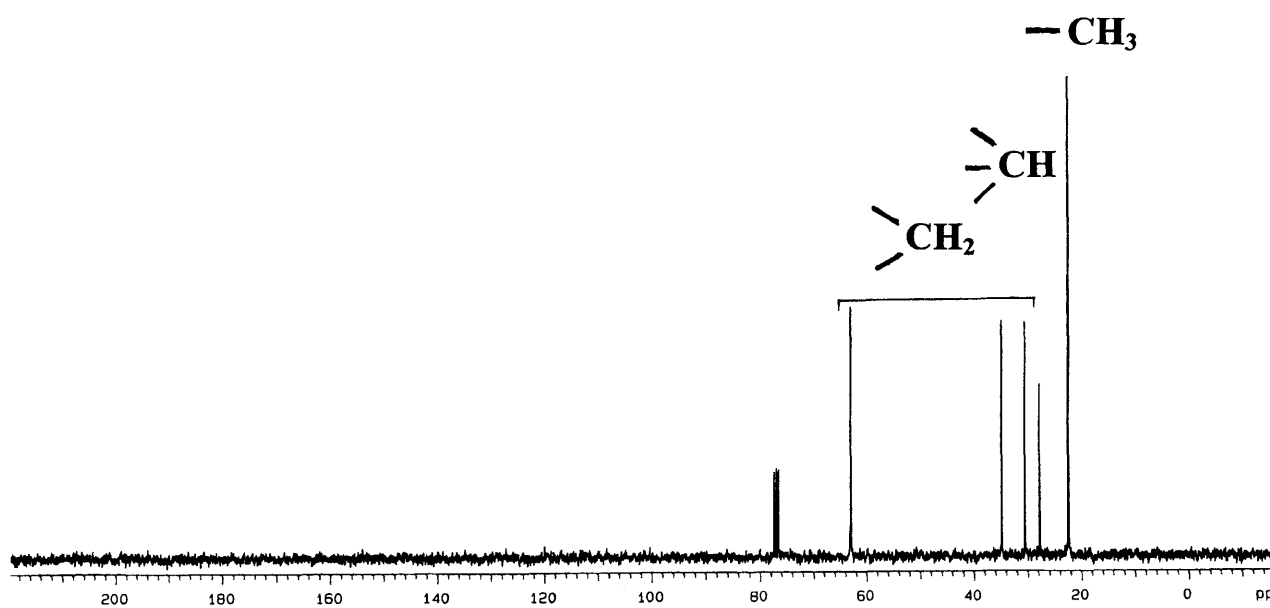




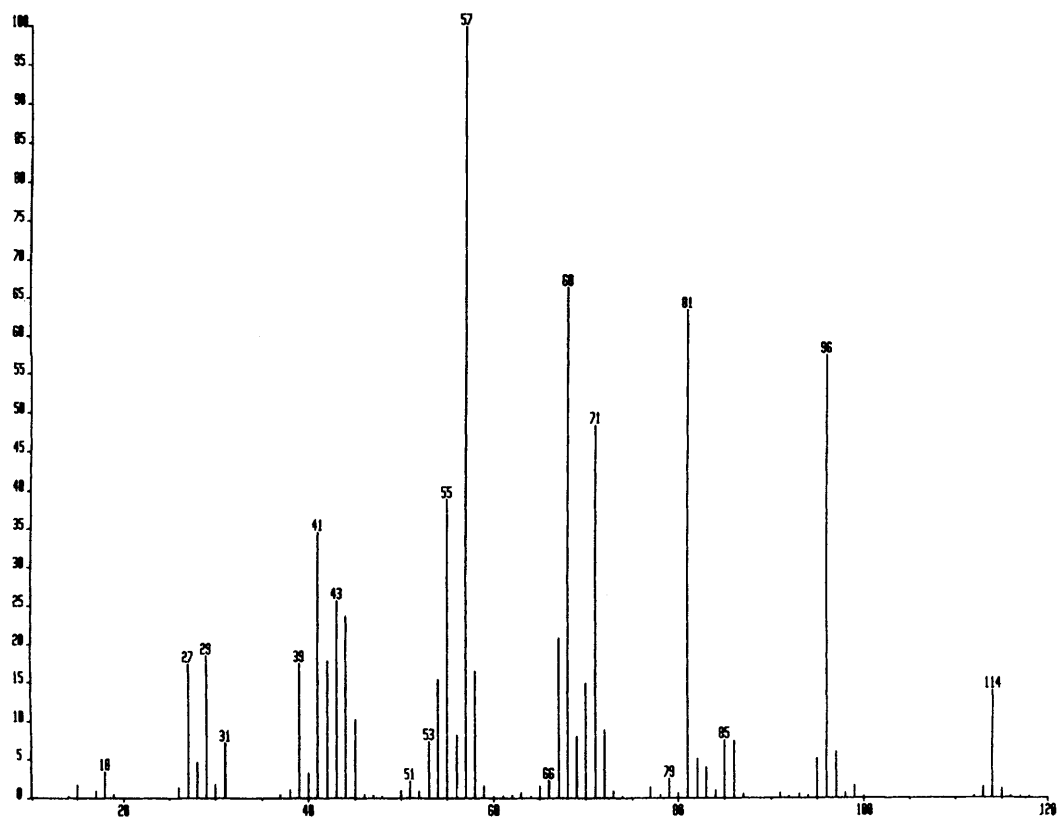
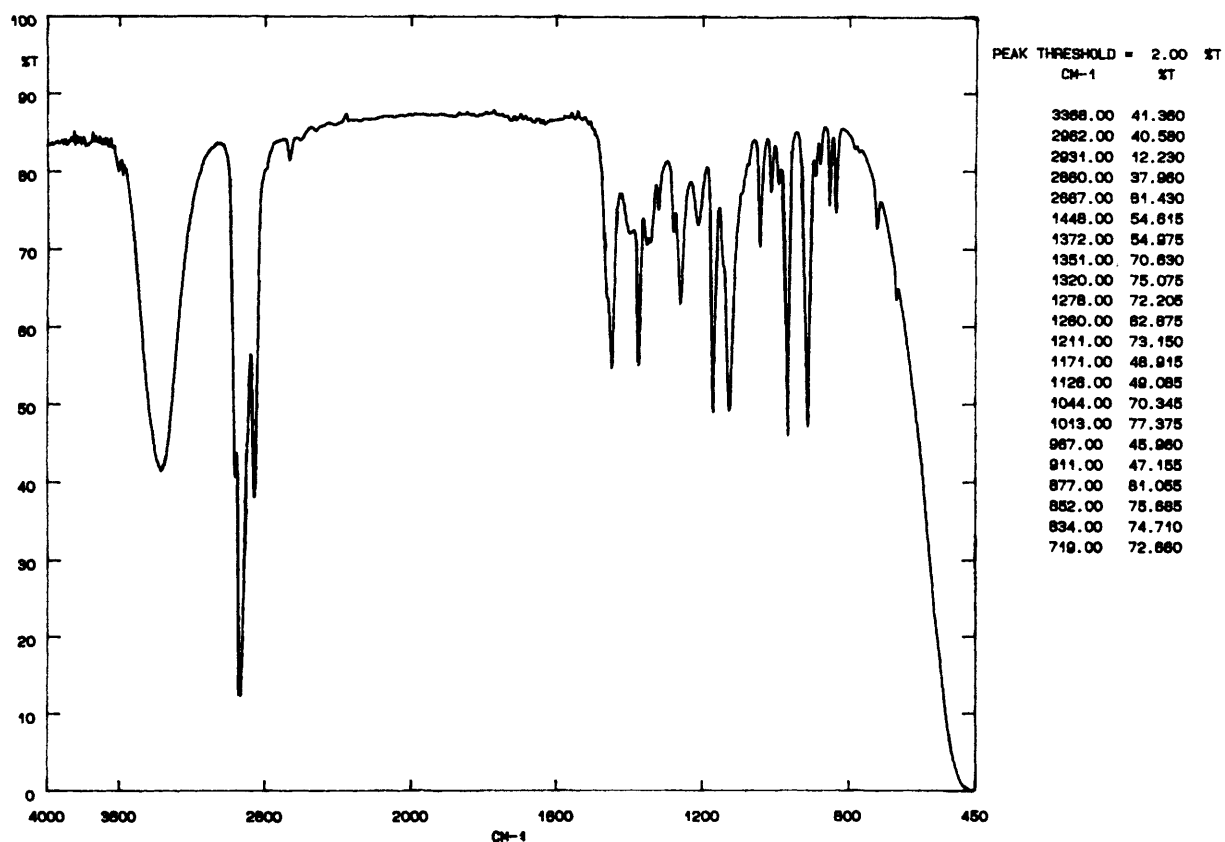
Sample 8.10 Continued



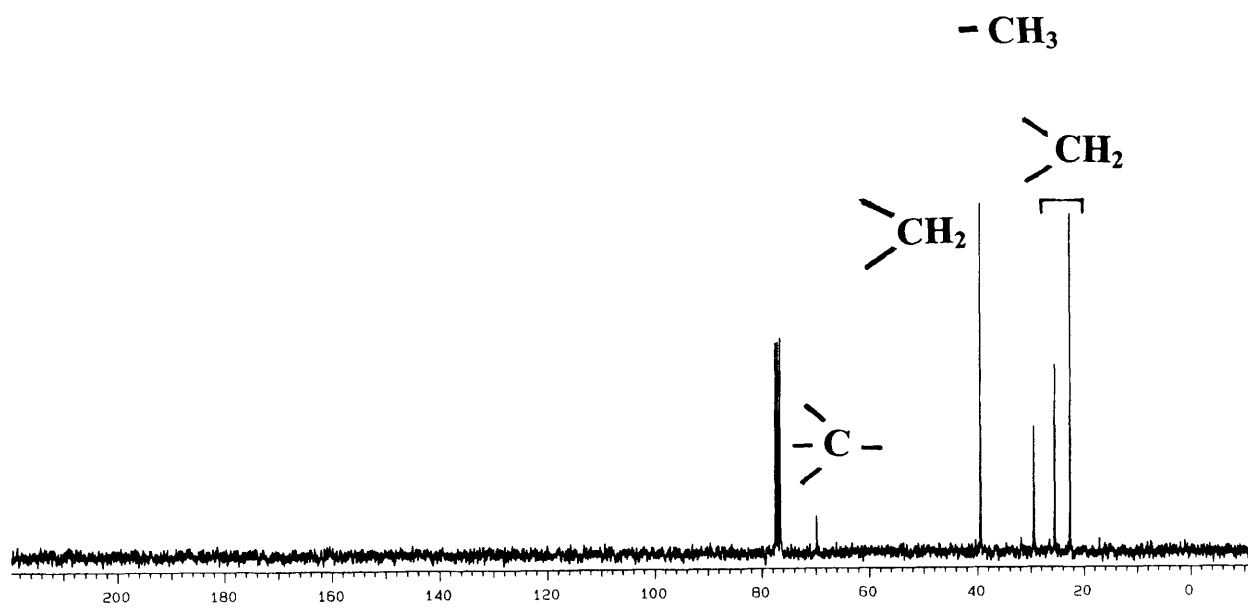
Sample 8.11

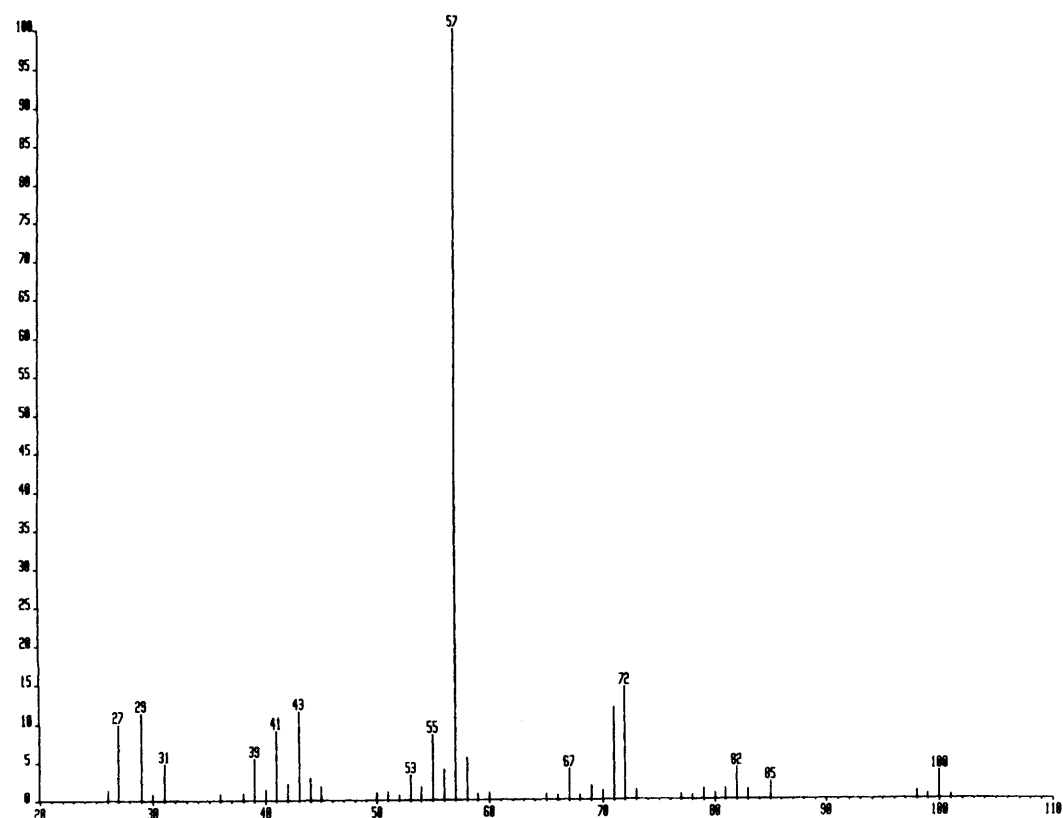
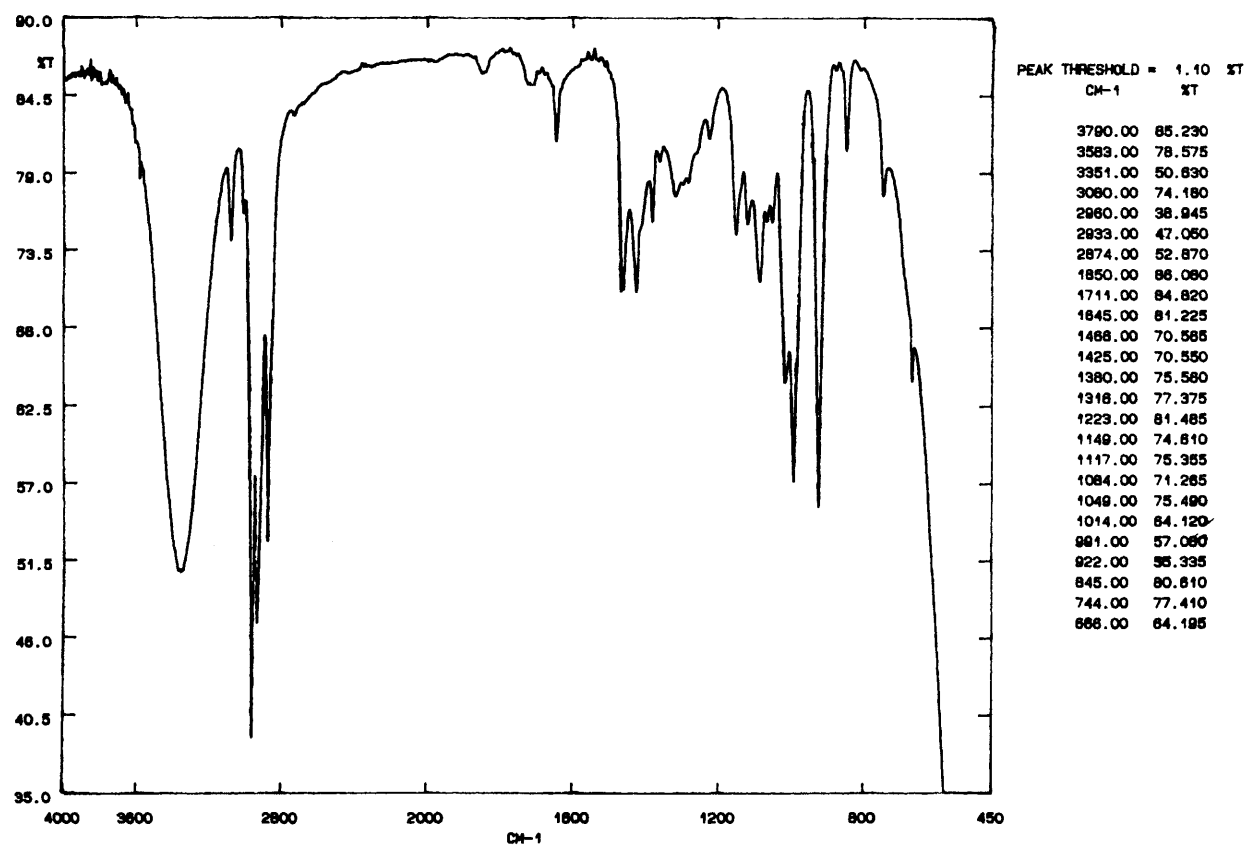


Sample 8.11 Continued

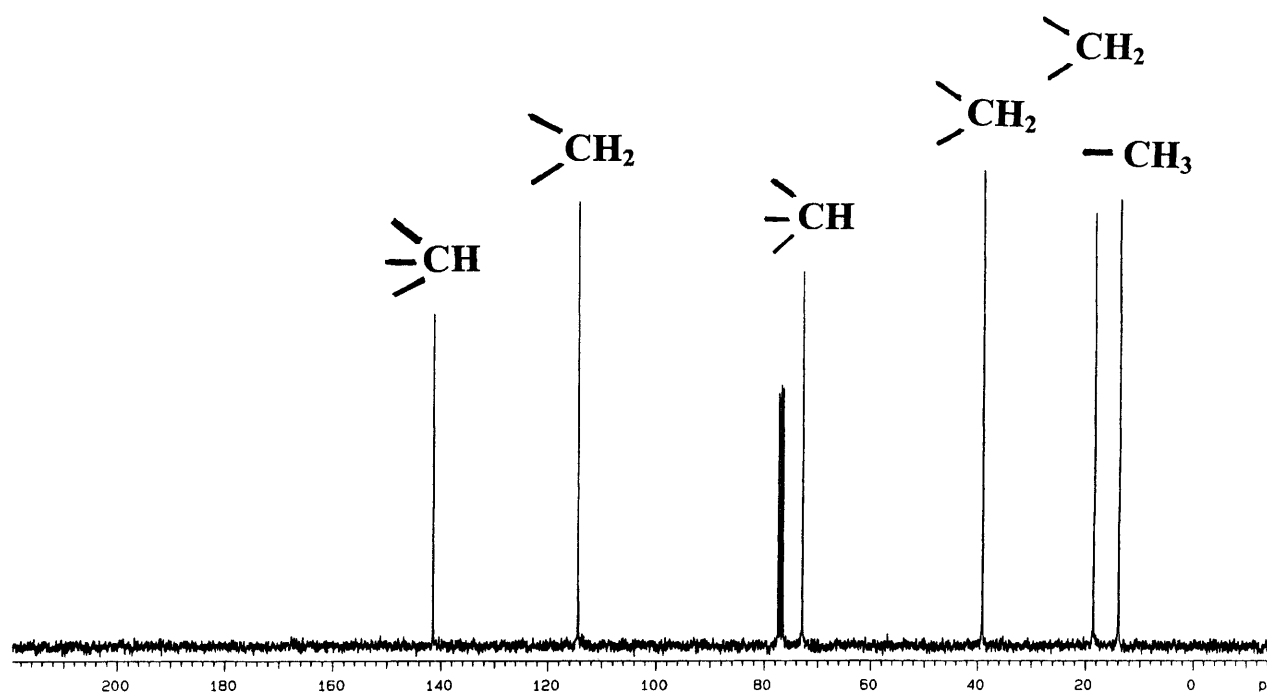


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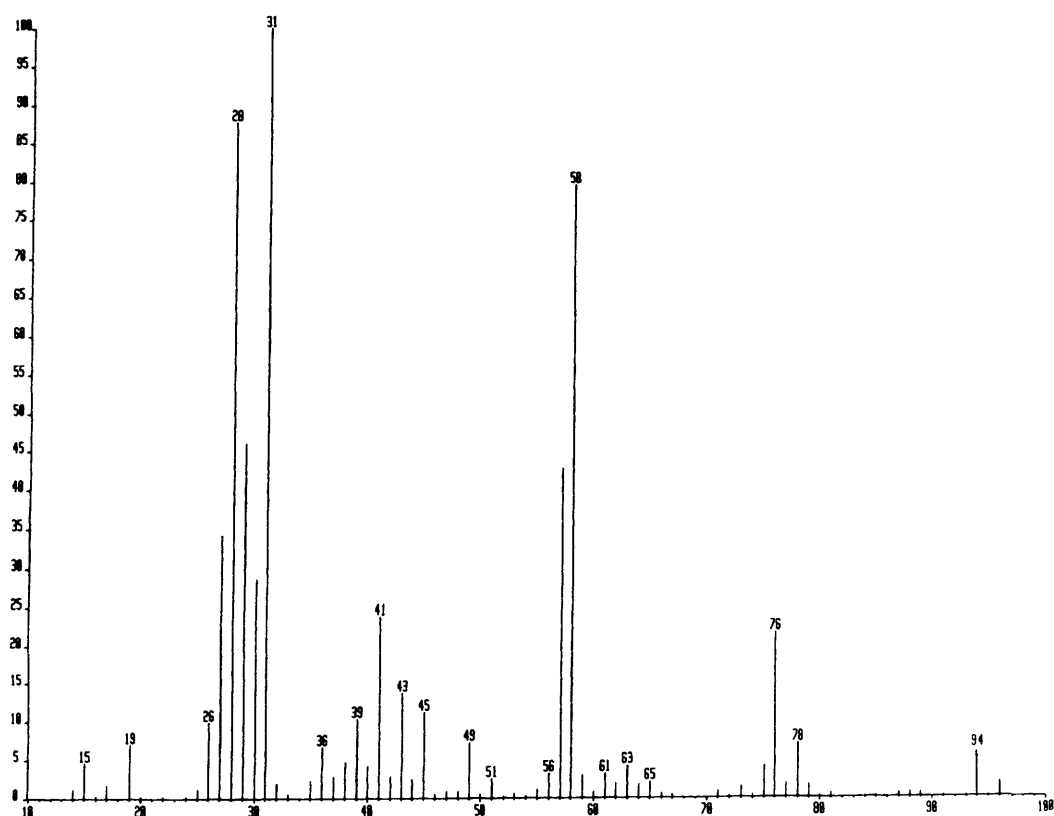
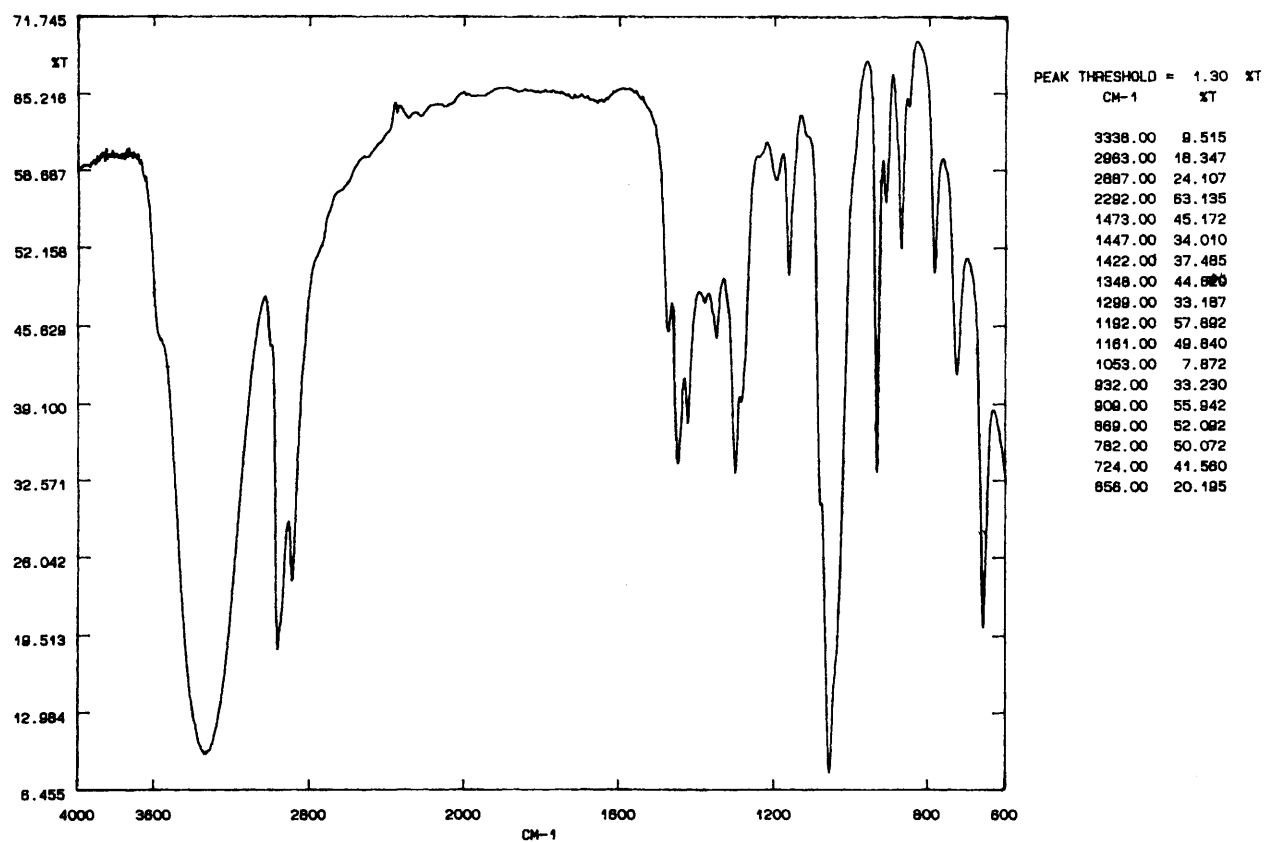
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Sample 8.13

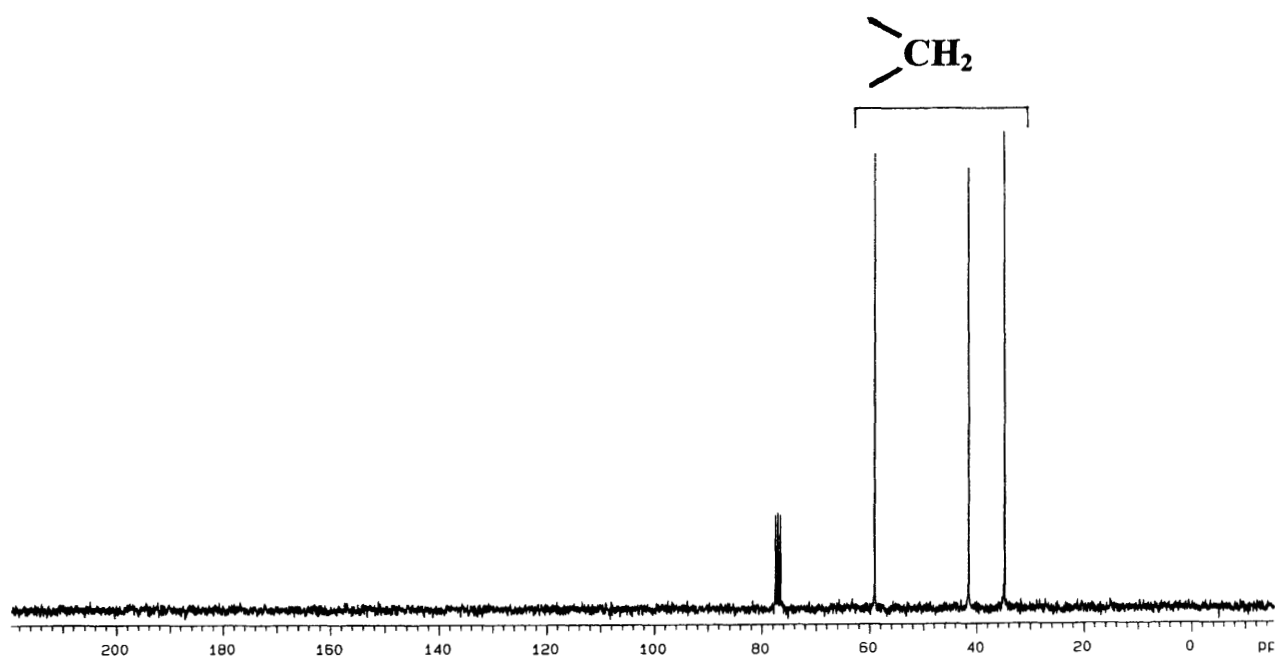


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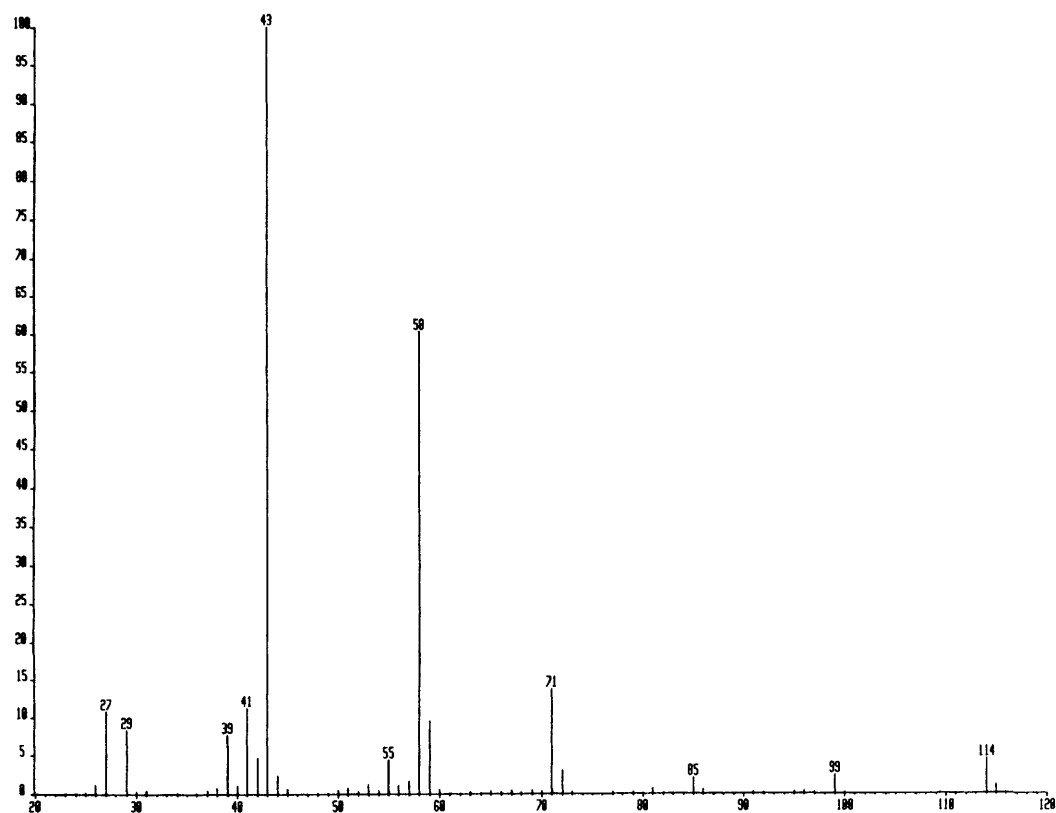
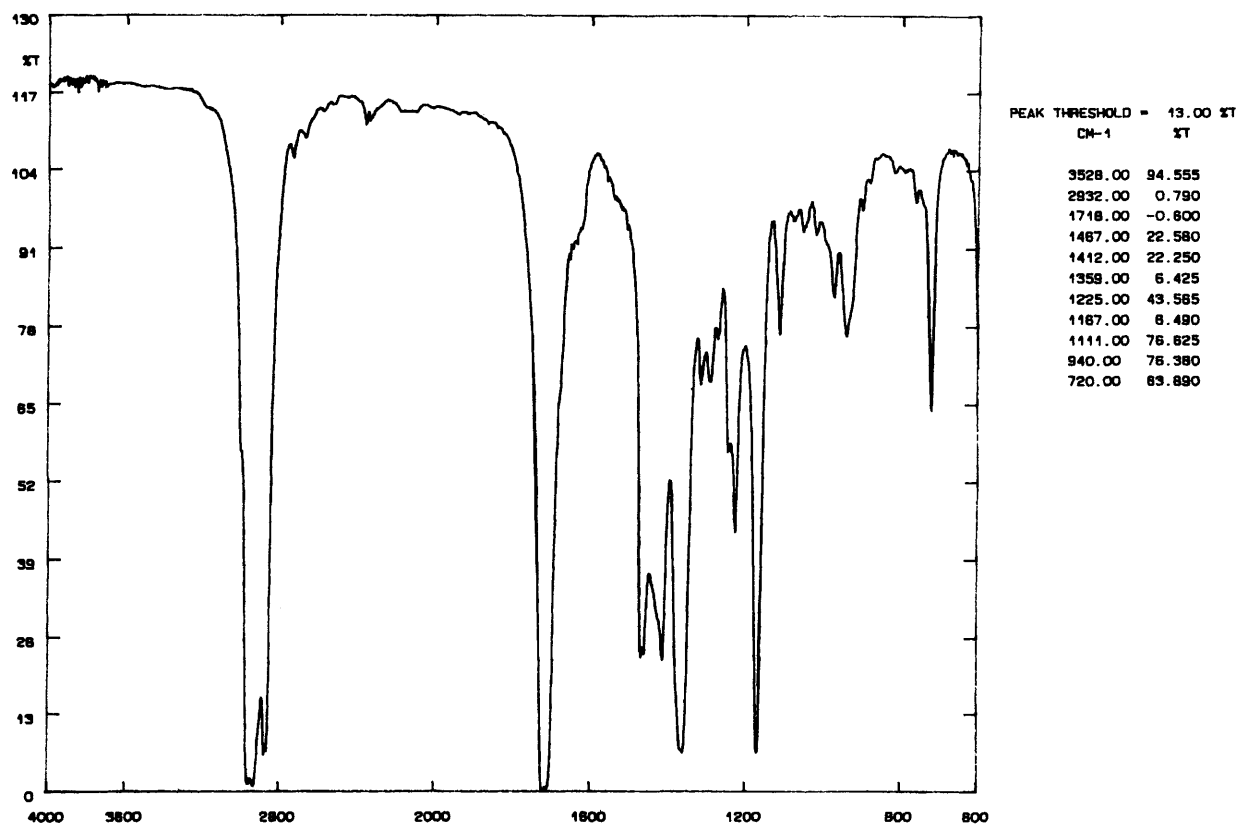


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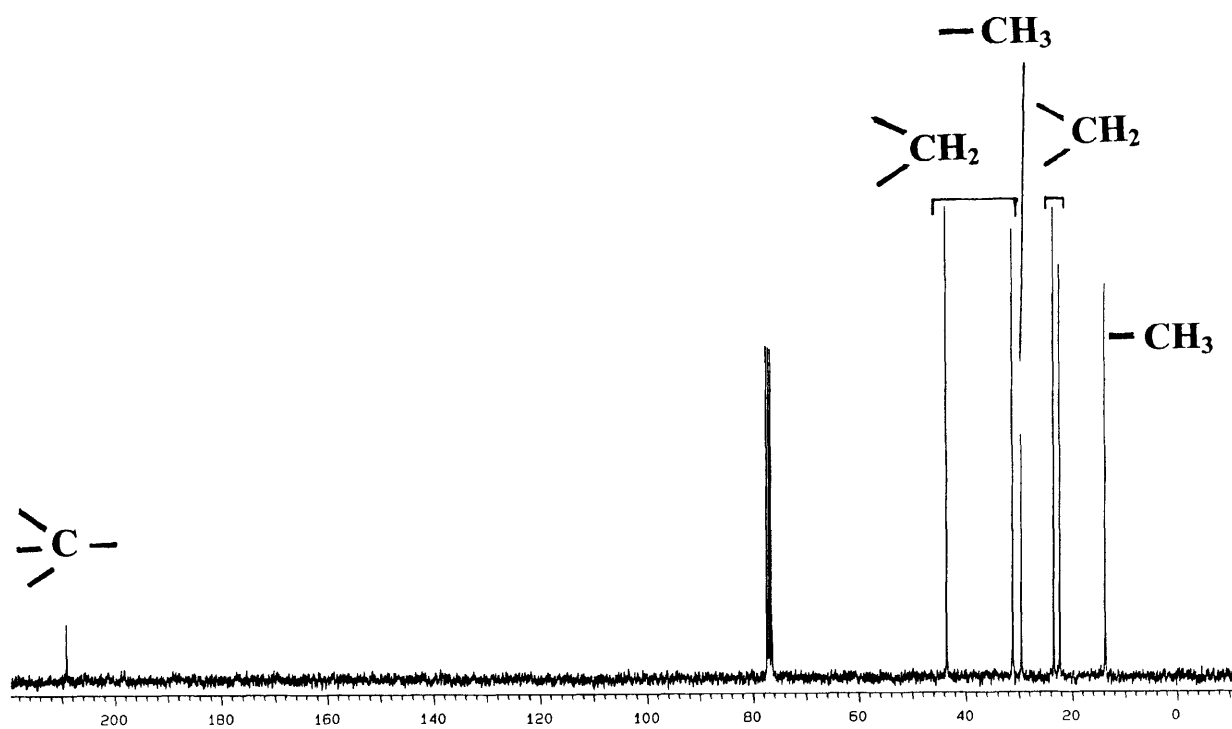




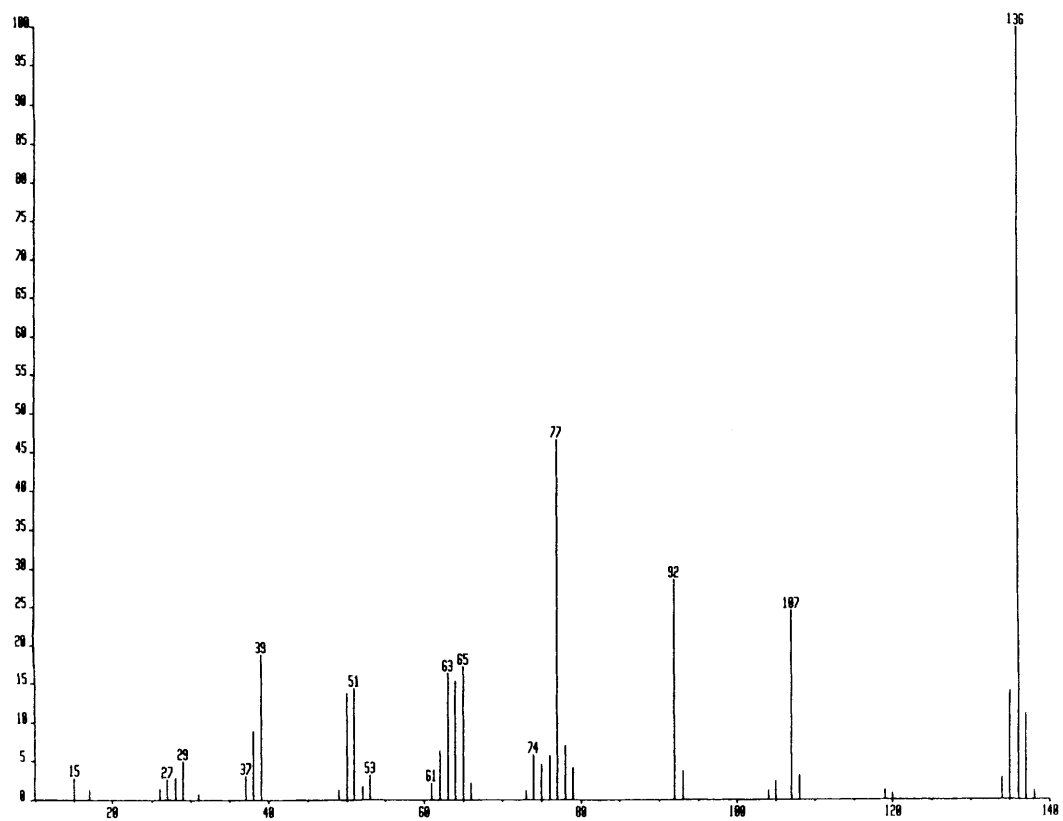
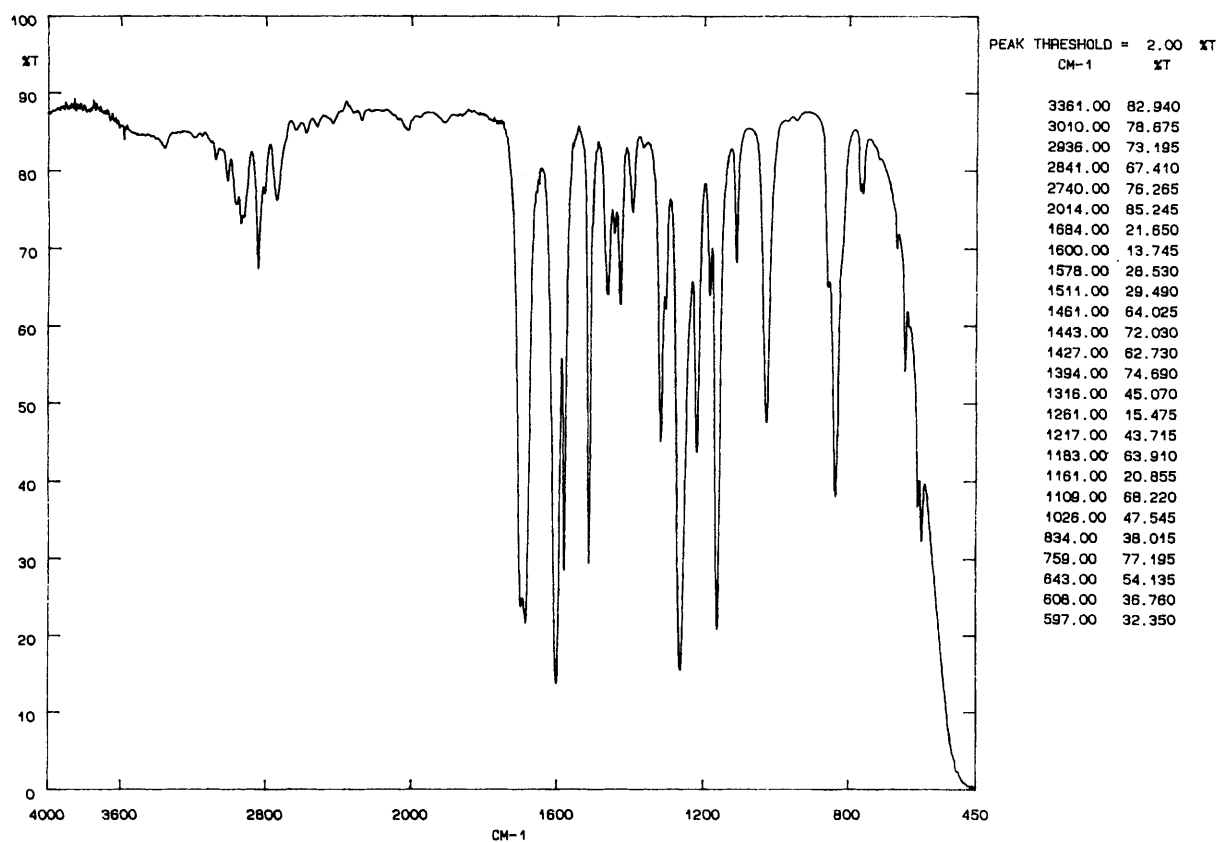
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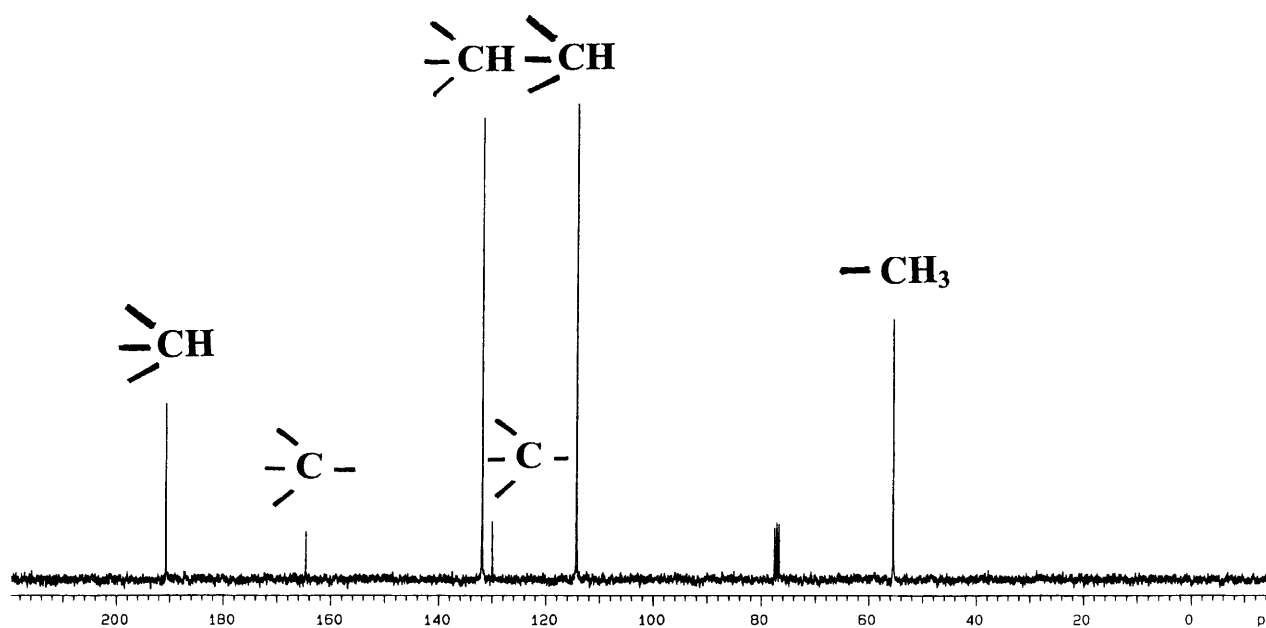
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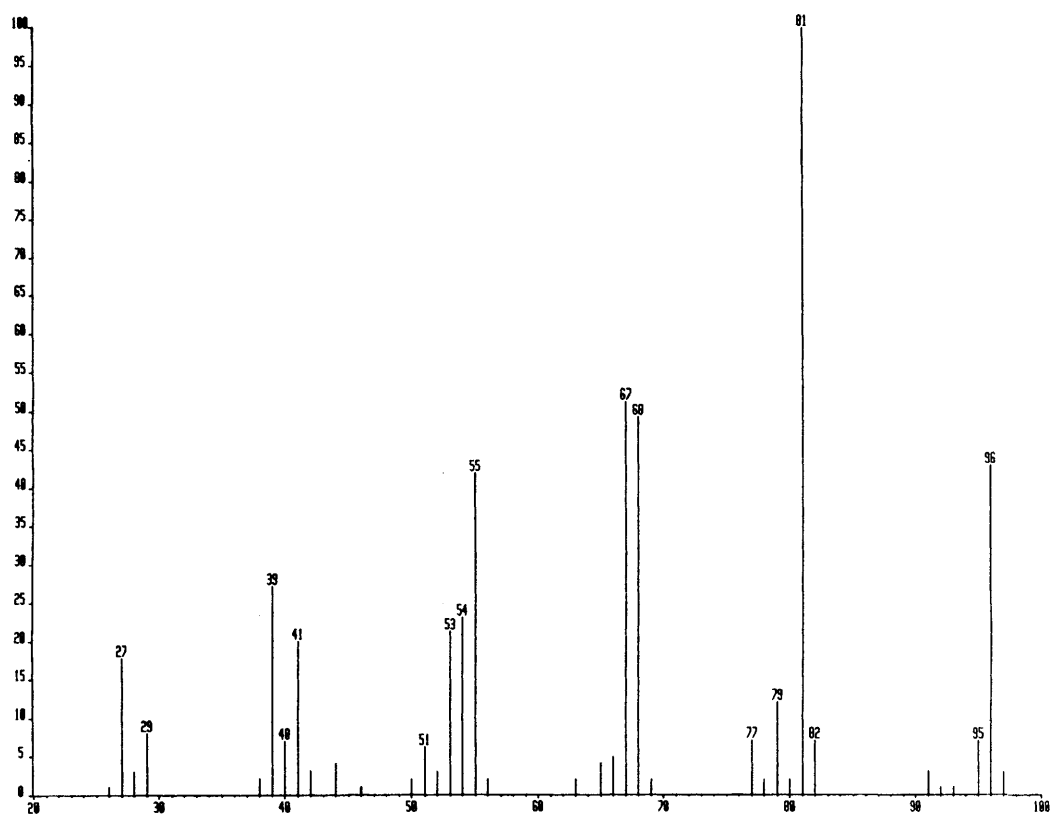
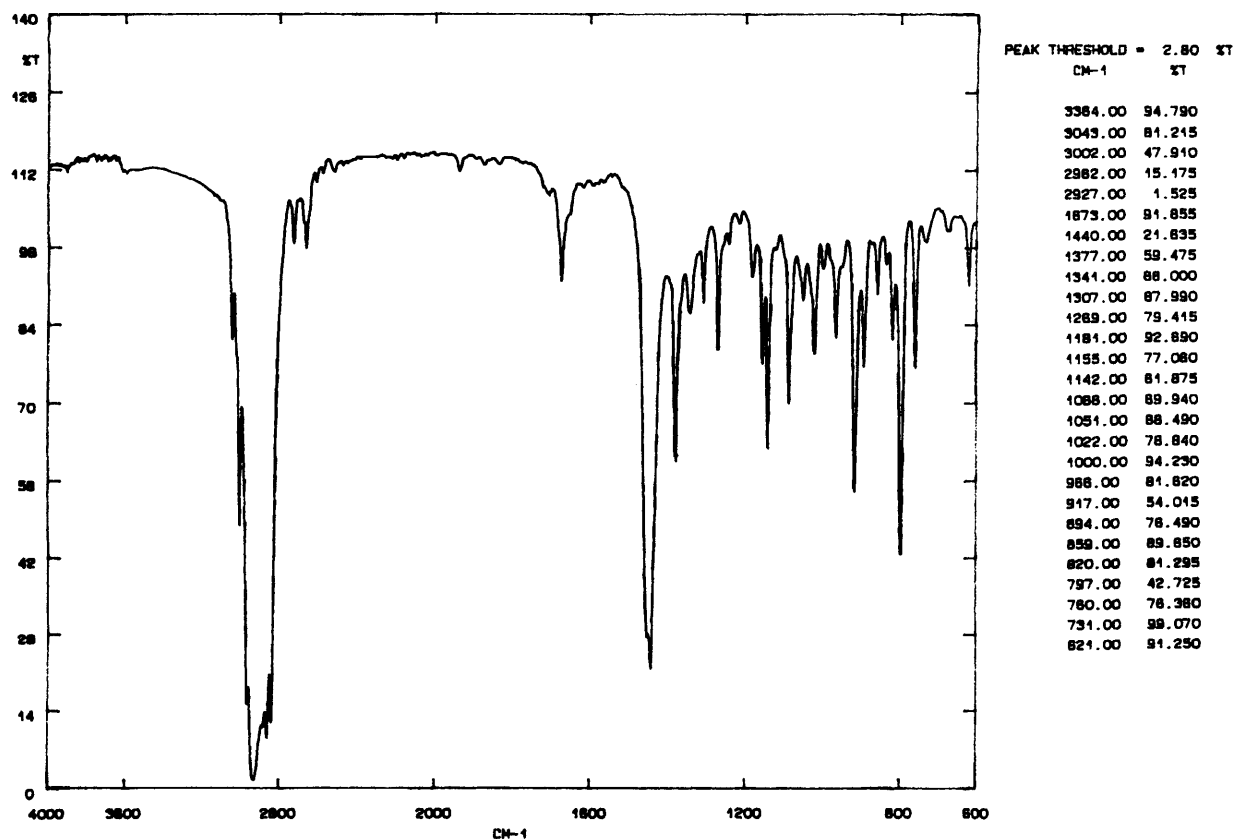
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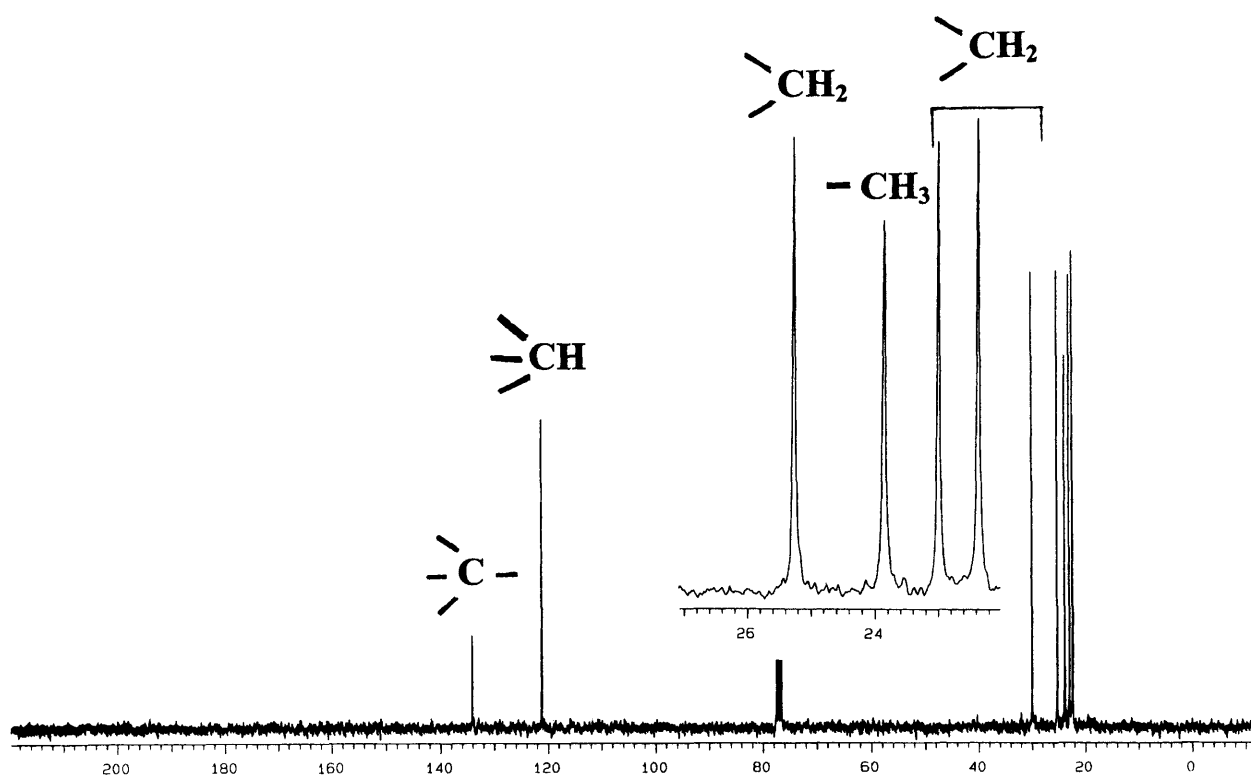
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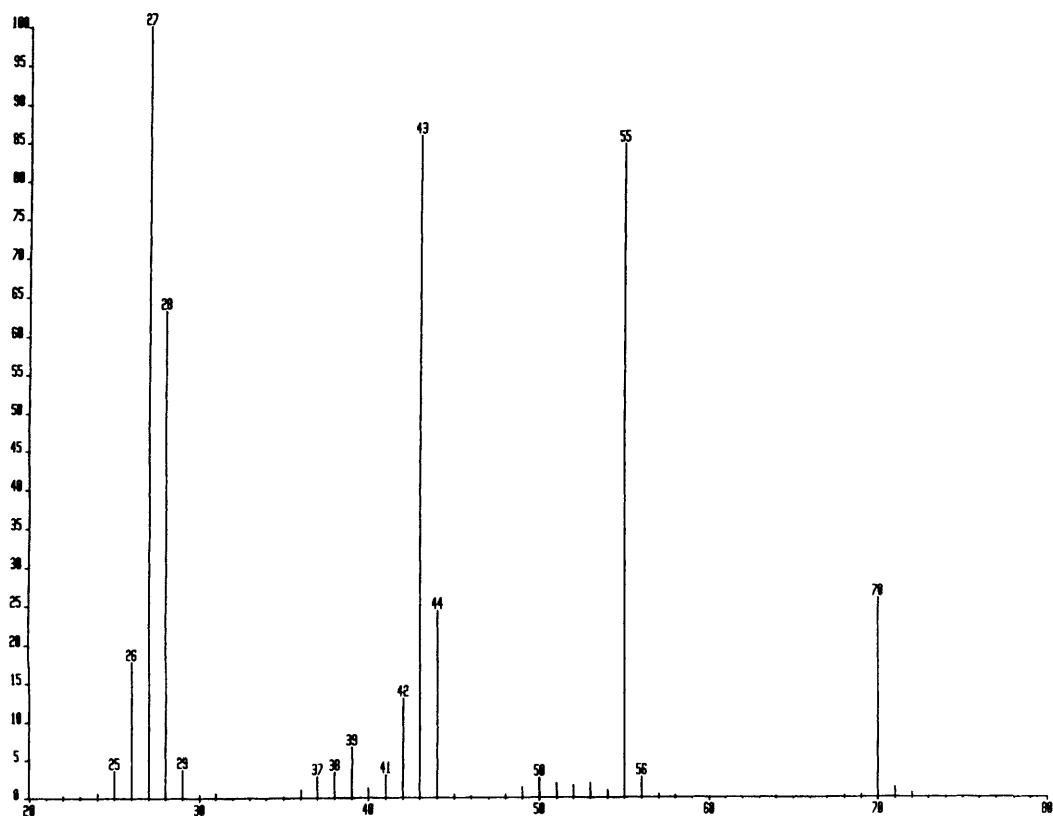
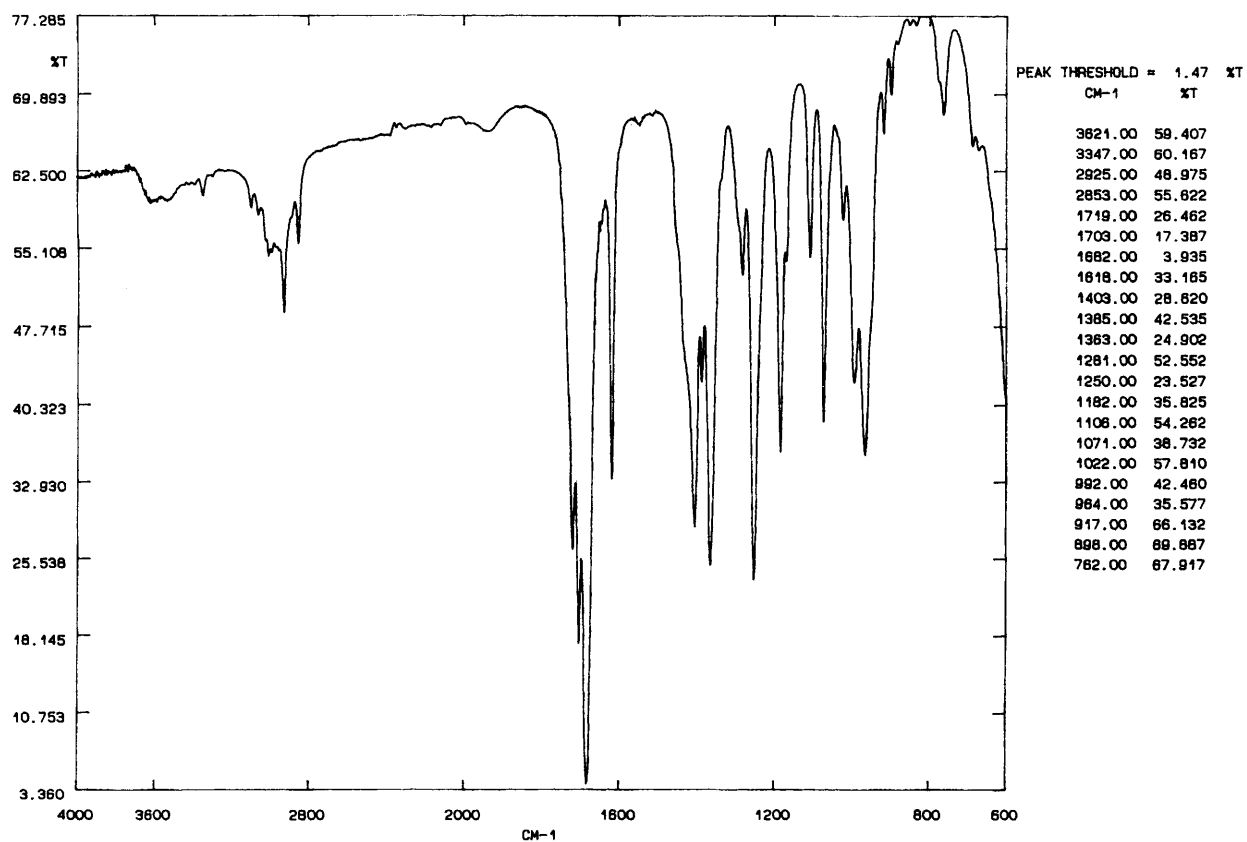
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Sample 8.17

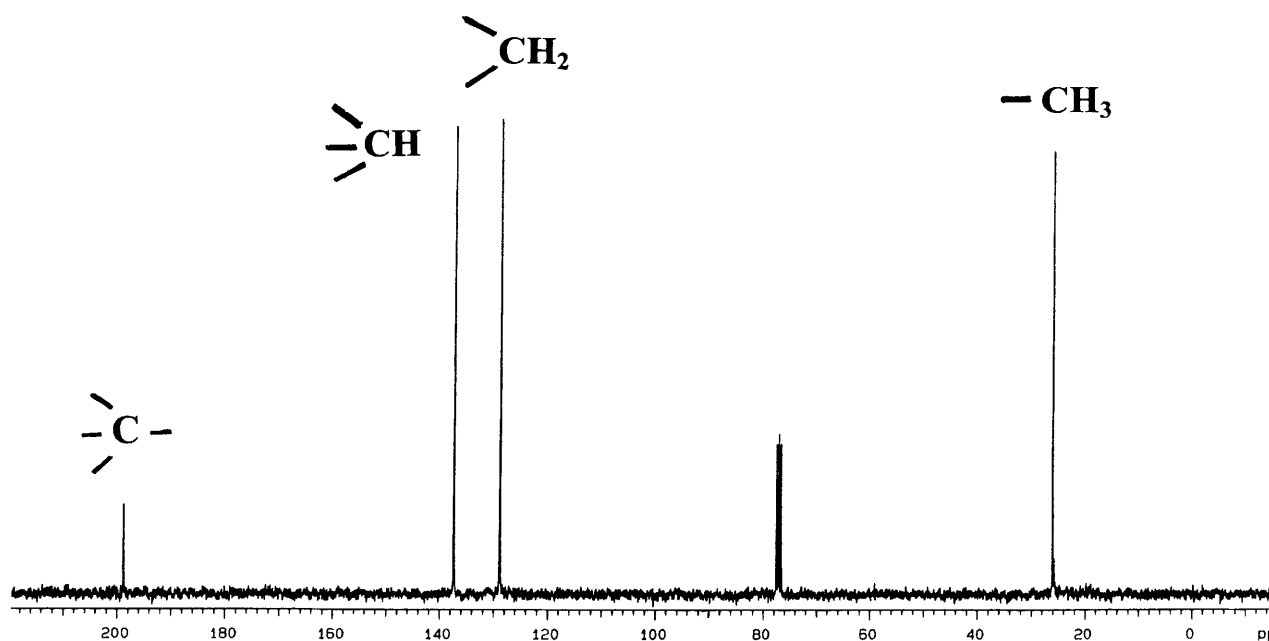


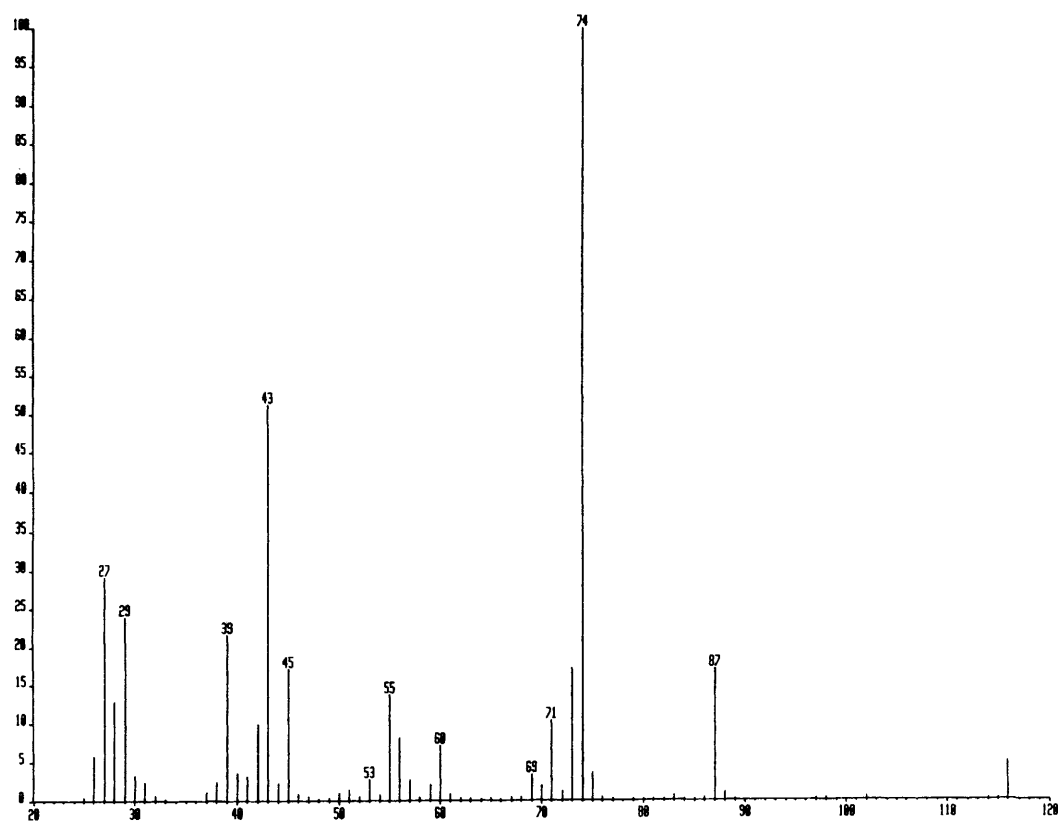
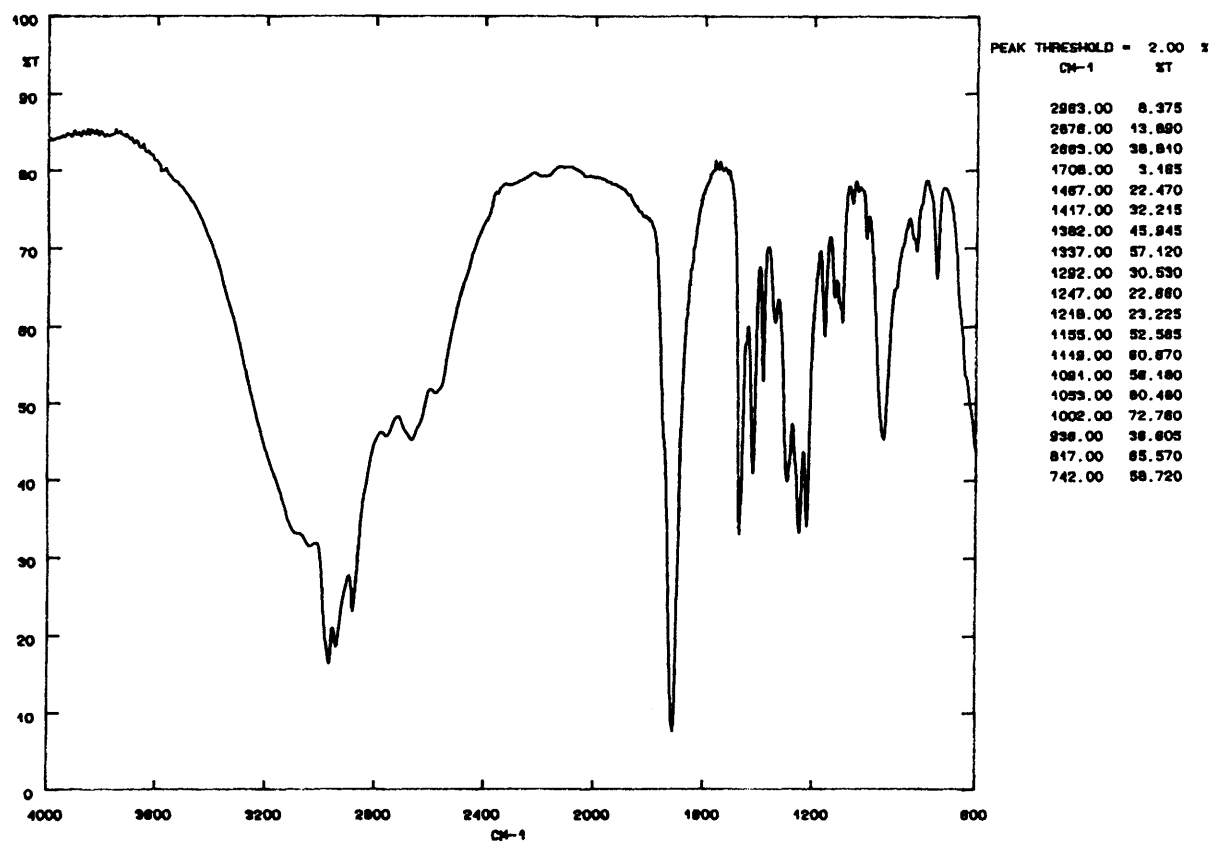
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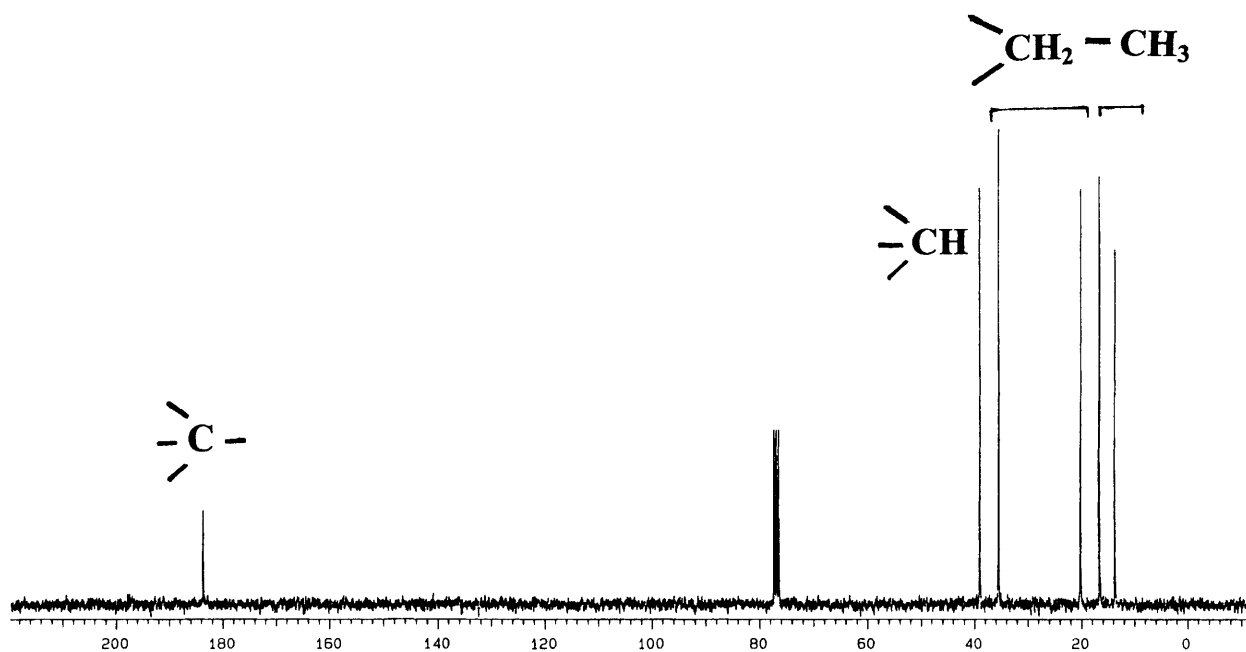
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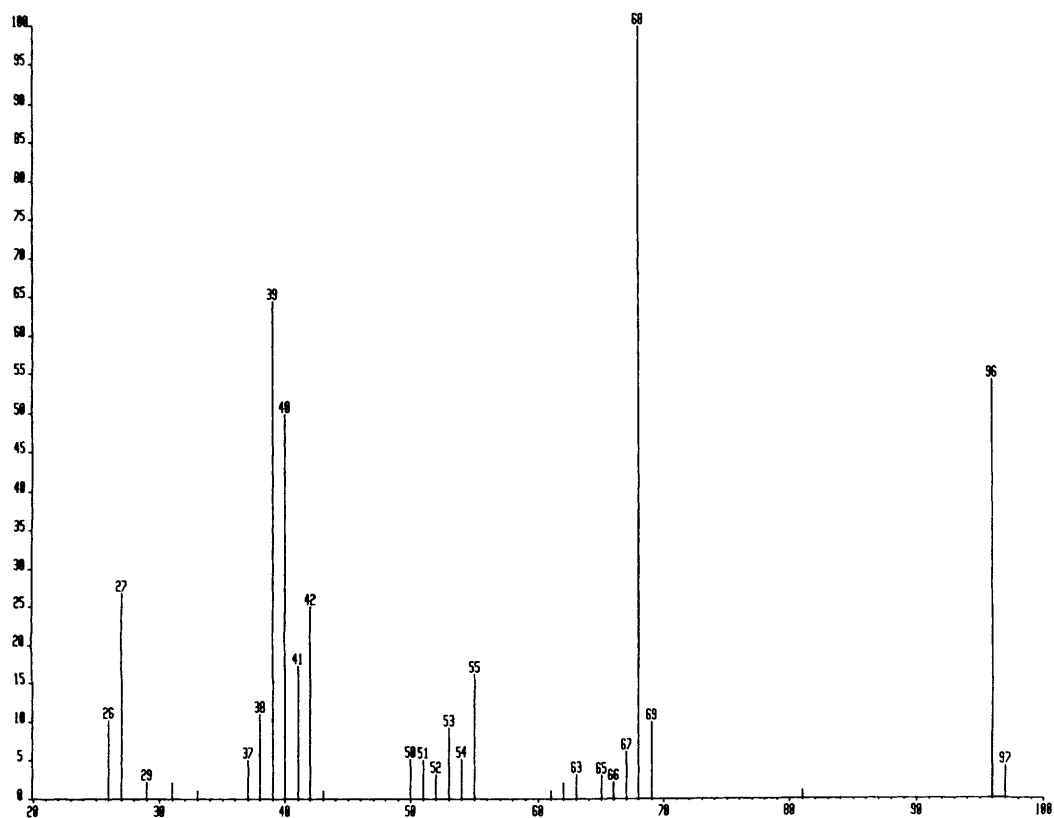
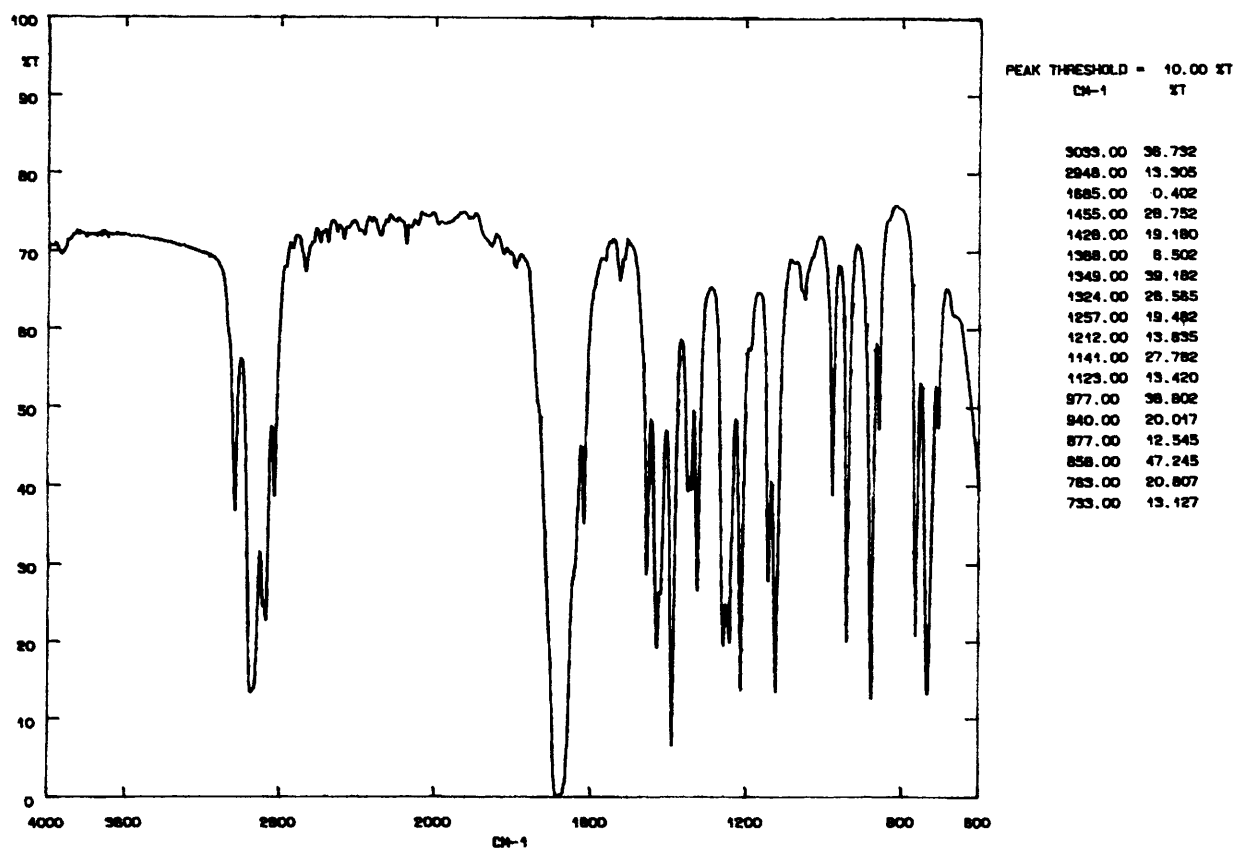


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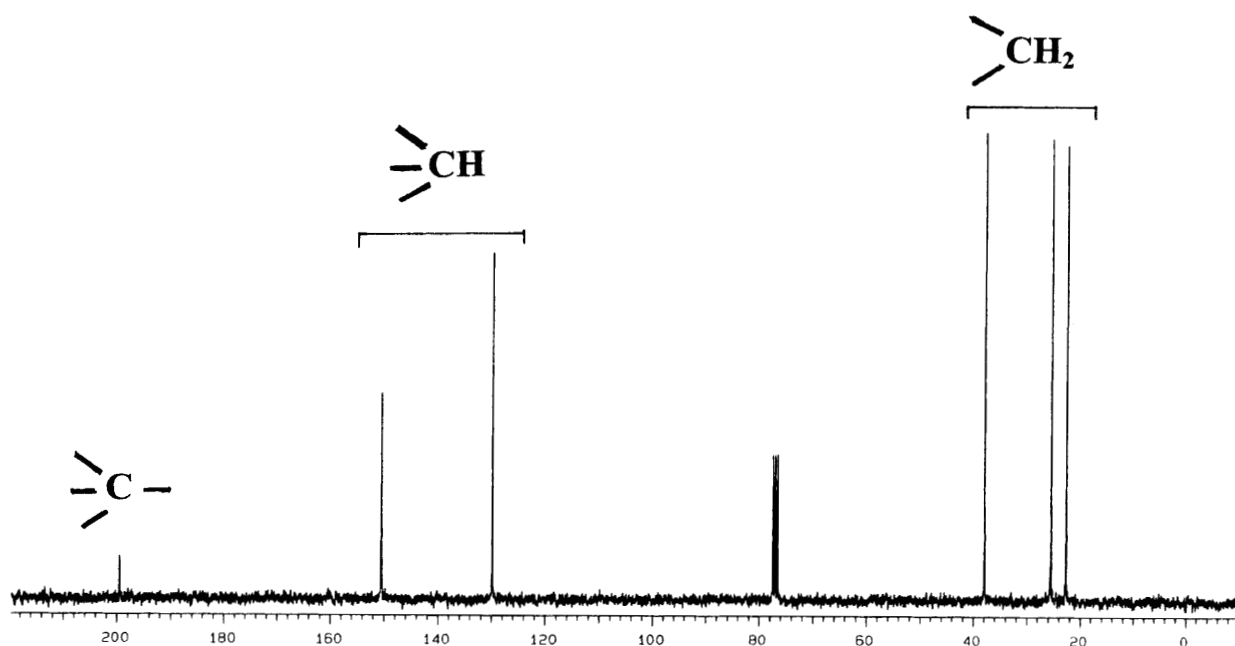
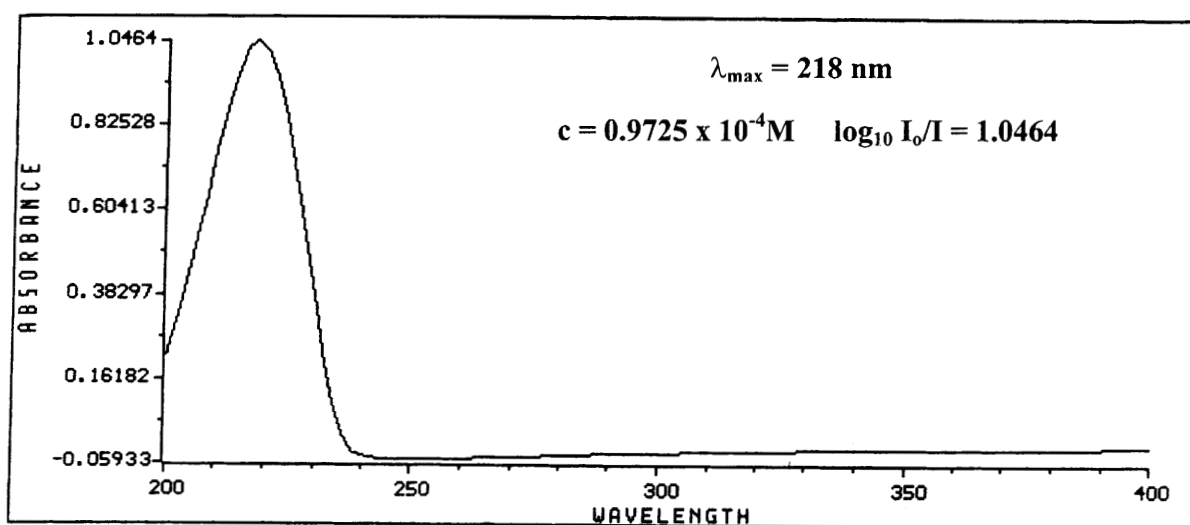
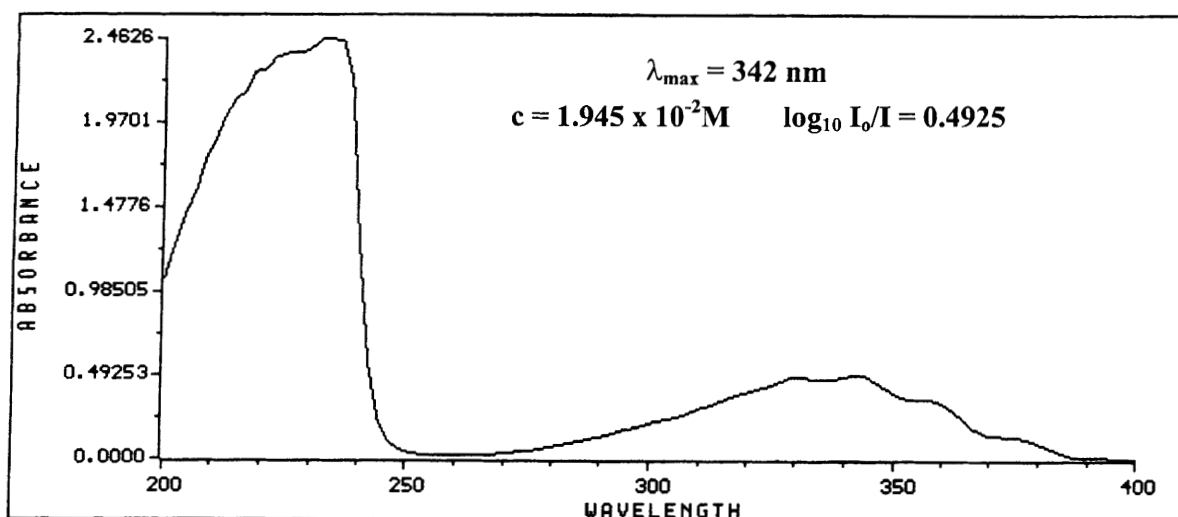


Sample 8.19

Sample 8.19 *Continued*



Sample 8.20



Sample 8.20 Continued



## **$^1\text{H}$ Nuclear Magnetic Resonance Spectroscopy**

$^1\text{H}$  nuclear magnetic resonance spectroscopy tells us about the environment of the hydrogen atoms in a molecule. The technique is based on exactly the same principles as  $^{13}\text{C}$  NMR spectroscopy: the  $^1\text{H}$  nucleus has nuclear spin  $\frac{1}{2}$ , so when placed in a strong magnetic field it can exist in higher or lower energy states. When the nucleus is irradiated, it absorbs radiofrequency radiation, and nuclei in lower energy spin states are promoted to higher energy spin states.

There are important differences between  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The main one is that the  $^1\text{H}$  atom, which has nuclear spin, comprises 99.98% of naturally occurring hydrogen. Consequently, most  $^1\text{H}$  NMR spectra can be measured by a single scan, and Fourier transform methods are used only in exceptional circumstances. This means that peak areas are proportional to the number of hydrogen atoms that the peak represents, and this is very valuable when analysing spectra.

Another important difference is that since  $^{12}\text{C}$ , the main carbon isotope, does not possess nuclear spin, most hydrogen atom spectra do not have any splitting from the carbon atom to which the hydrogen is attached. The few hydrogen atoms which are attached to  $^{13}\text{C}$  atoms and hence are split produce tiny peaks which are usually lost in the background electronic noise on the spectrum. Consequently, we need consider only  $^1\text{H}$  to  $^1\text{H}$  coupling, unless we have present other atoms with nuclear spin such as fluorine or phosphorus.

As in  $^{13}\text{C}$  NMR, the frequency of the radiation absorbed by a  $^1\text{H}$  nucleus depends only on the magnetic field in which the  $^1\text{H}$  nucleus is placed. When a spectrum is measured, this field has three components:

- A. The main component, the applied field, which is very large, acts equally on all atoms.
- B. The field resulting from the electron density around each nucleus. Movement of these electrons in the applied magnetic field generates a field which opposes the applied field, moving the absorption frequency of a neighbouring nucleus downfield. The effects produced on the  $^1\text{H}$  nucleus absorption are similar to but smaller than those produced on  $^{13}\text{C}$  absorption. The  $^{13}\text{C}$  NMR absorption of neutral atoms covers a range of  $\delta 200$ ; the range of  $^1\text{H}$  absorptions is approximately  $\delta 10$ . Thus, the shift of absorption frequency, known as chemical shift, on a  $^1\text{H}$  atom due to an electronegative neighbour is approximately 5% of the chemical shift on a similarly placed  $^{13}\text{C}$  atom. A list of chemical shifts is given in Tables 9.1 and 9.2.

There is a problem with chemical shifts of the hydrogen atoms of groups such as  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{SH}$  and  $-\text{COOH}$ , where the hydrogen atoms undergo rapid exchange with each other and with traces of water

**Table 9.1**  $^1\text{H}$  NMR chemical shifts of hydrogen atoms attached to carbon atoms in different environments

Group	$^1\text{H}$ chemical shift ( $\delta$ )	
	Attached to groups of low electronegativity	Full range
$\text{CH}_3$	0.9	0.9–3.8
$\text{CH}_2$	1.4	1.4–4.3
$\text{CH}$	1.5	1.5–4.5
$\text{C}\equiv\text{C}-\text{H}$	1.8	1.8–3.1
$\text{C}=\text{C}-\text{H}$	5.2	4.5–6.0
Ph	7.3	6.0–9.0
$\text{H}-\text{C}=\text{O}$	9.8	9.5–10

**Table 9.2** Effect of electronegative groups on  $^1\text{H}$  NMR chemical shifts

Group	Chemical shift ( $\delta$ ) when attached to					
	Alkyl	Aryl	$\text{C}=\text{O}$	$\text{C}=\text{C}$	$-\text{OH}$	$-\text{O}-\text{C}=\text{O}$
$\text{CH}_3$	0.9	2.3	2.0–2.2	2.0	3.5	3.7
$\text{CH}_2$	1.4	2.7	2.2–2.4	2.4	3.6	4.1
$\text{CH}$	1.5	3.0	2.5–2.7	2.7	3.9	4.8

present in the sample. The exchange is faster than the measurement of absorption of radiation, so we get a single peak for the exchanging atom and the water, whose chemical shift is a weighted average of the chemical shifts of the atoms involved. Such peaks can readily be identified by a procedure known as a ‘ $\text{D}_2\text{O}$  shake’. A drop of deuterium oxide is added to the sample in the NMR tube, and the tube shaken briefly. The exchangeable hydrogen of the sample exchanges rapidly with deuterium. The  $\text{H}_2\text{O}$  generated, and the  $\text{D}_2\text{O}$ , float on top of the solvent, outside the region where the spectrum is being measured. The  $\text{OH}$  or similar peak thus disappears, as can be seen by comparing Figures 9.1 and 9.2.

The chemical shifts of  $\text{OH}$  groups do give some useful structure information. As a rough rule, alcohol  $\text{OH}$  peaks are found in the range  $\delta 0$  to 5, phenolic  $\text{OH}$  peaks in the range  $\delta 5$  to 10, and carboxylic acid  $\text{COOH}$  peaks in the range  $\delta 10$  to 15.

- C. The field resulting from the magnetic field of neighbouring nuclei. This has the effect of the signal from a  $^1\text{H}$  atom being split by the magnetic fields of neighbouring nuclei, and provides the most valuable information from a  $^1\text{H}$  NMR spectrum, as well as providing most of the problems.

The main  $^1\text{H}$  to  $^1\text{H}$  splitting of the absorption peak of a  $^1\text{H}$  nucleus is by the magnetic fields of  $^1\text{H}$  atoms on neighbouring carbon atoms. There can be small splittings from hydrogen atoms on the next but one carbon atom, but these are usually observed only in rigid systems, such as alkenes and cyclic systems. Splitting is always mutual; if  $\text{H}_\text{A}$  splits  $\text{H}_\text{B}$ , then  $\text{H}_\text{B}$  must split  $\text{H}_\text{A}$ .

Provided we have free rotation around the  $\text{C}-\text{C}$  bonds, the splitting patterns in  $^1\text{H}$  to  $^1\text{H}$  coupling are similar to those we have met when considering  $^1\text{H}$  to  $^{13}\text{C}$  coupling. The  $(n+1)$  rule applies: a peak is split into  $(n+1)$  peaks if it has  $n$  hydrogen atoms on neighbouring carbon atoms. Thus, a single hydrogen



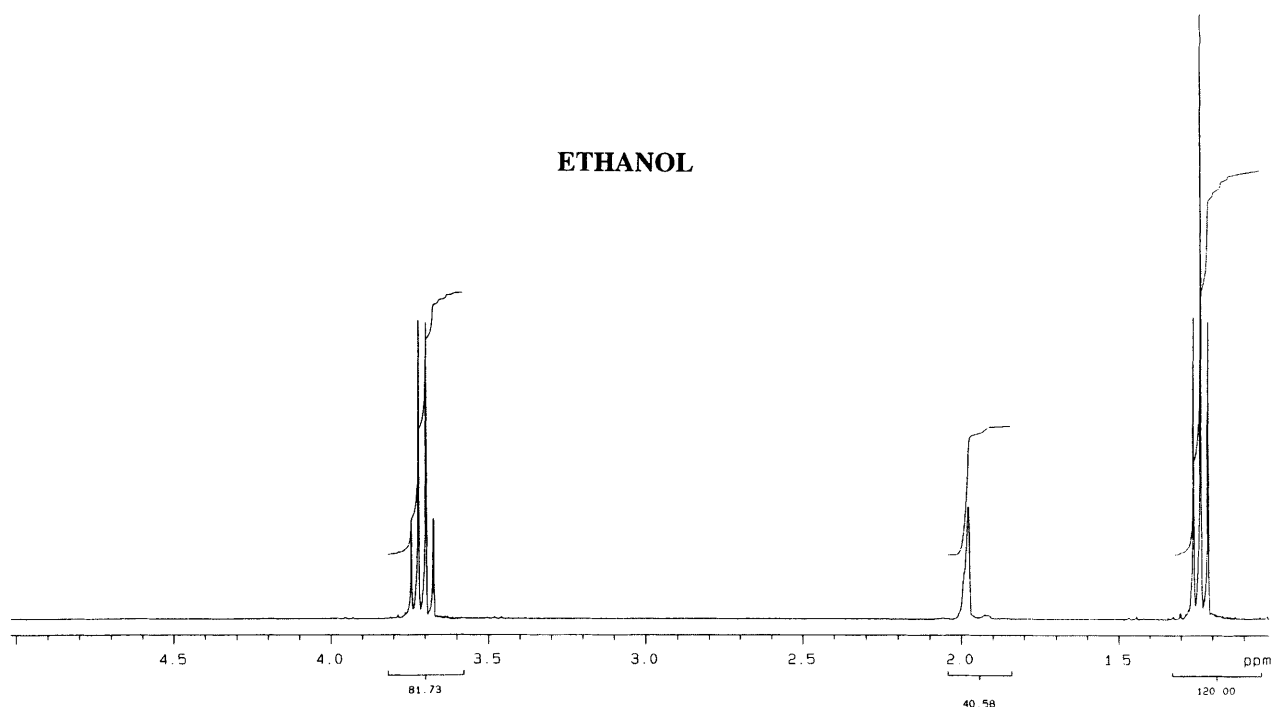


Figure 9.1

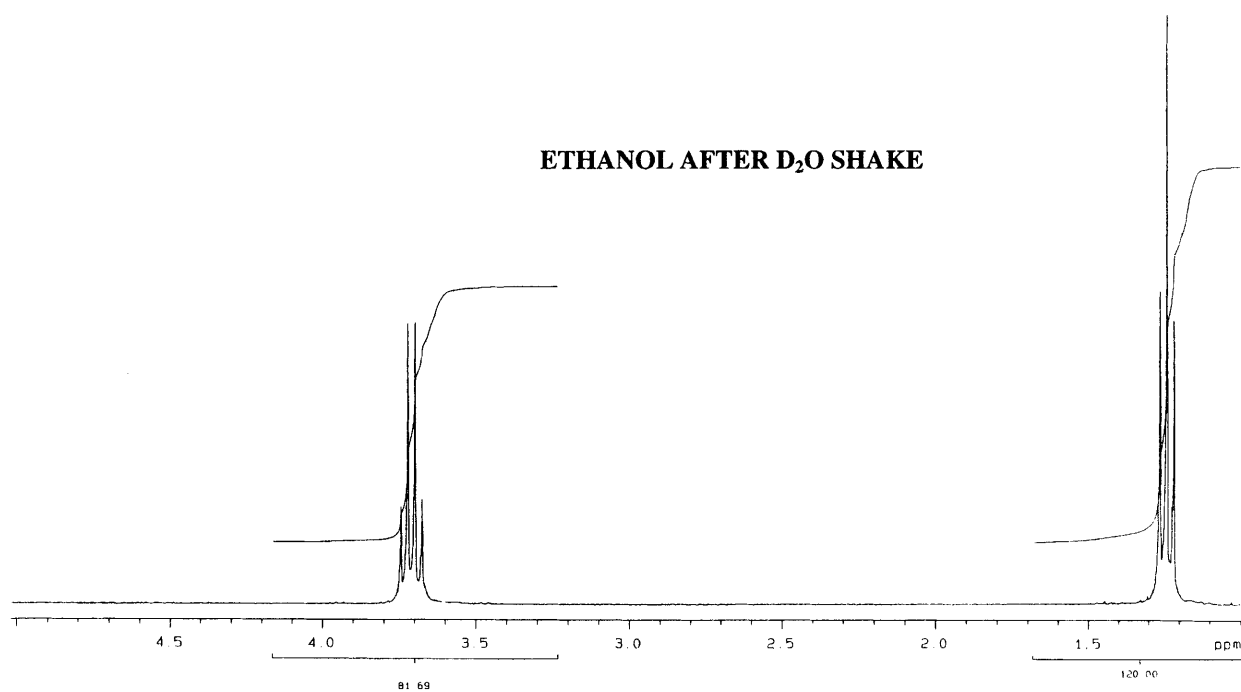


Figure 9.2

atom on a neighbouring carbon atom splits a  $^1\text{H}$  signal into a doublet, two split it into a triplet, three into a quartet, up to the rare situation of nine atoms splitting a neighbouring atom absorption into ten peaks. Simple splittings are illustrated in Diagram 9.1.

These patterns depend on the assumption that the size of the splitting, expressed as the coupling constant,  $J$ , is the same for all couplings. The coupling constant depends on the dihedral angle between the carbon to

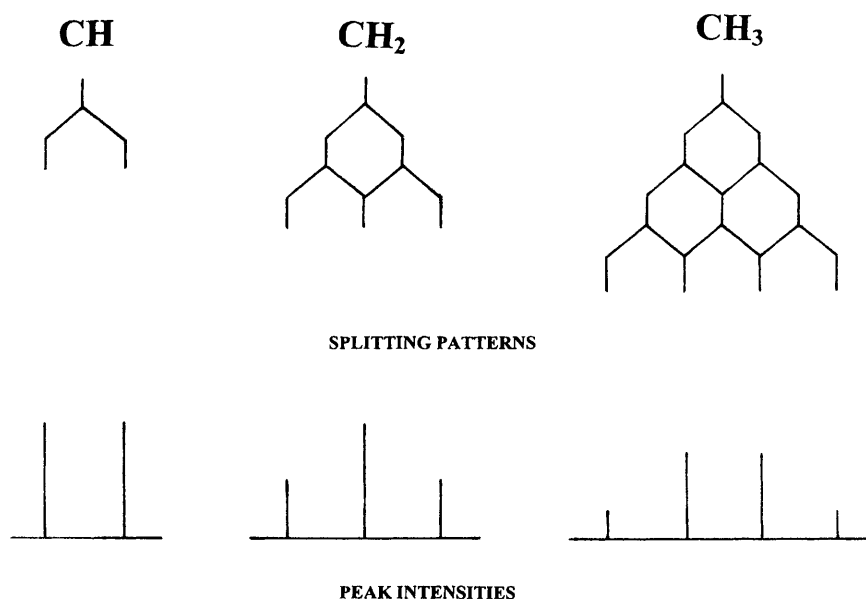
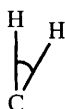
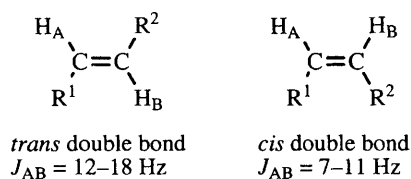


Diagram 9.1

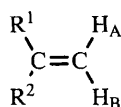
hydrogen bonds of the two hydrogen atoms involved. Looking along the C–C bond, we can see this angle:



In any system in which we have free rotation of C–C bonds, the dihedral angle varies rapidly during measurement of absorption, so we see only an averaged value of  $J$  for all couplings and the patterns shown in Diagram 9.1 are observed. In rigid systems,  $J$  can vary over the range from 0 to 20 Hz and more complex patterns are observed.  $J$  values can be very useful, for example, in telling us if vicinal hydrogen atoms on a double bond are *cis* or *trans* to each other:

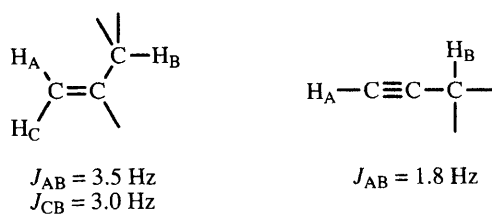


We also get geminal coupling if we have a =CH<sub>2</sub> group:



The  $J$  value is now dependent on the electronegativities of R<sup>1</sup> and R<sup>2</sup>.

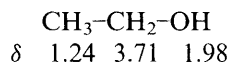
In rigid systems such as these, we can also get long range coupling:



The coupling constant is easily measured: it is the difference, in Hz, of the frequencies of absorption of the peaks produced by the splitting. It is independent of the applied field. If we have a regular multiplet, as shown in Diagram 9.1, then all the coupling constants are the same, and are given by the difference in absorption frequency of any pair of neighbouring peaks in the multiplet.

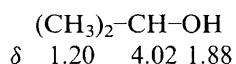
Like <sup>13</sup>C NMR spectra, <sup>1</sup>H NMR spectra are measured in solution, usually in CDCl<sub>3</sub>, since it does not contain any hydrogen and so does not produce a <sup>1</sup>H NMR signal. Any residual CHCl<sub>3</sub> produces a peak at δ7.25. The solution is placed in a thin walled glass tube, and spun in a powerful magnetic field. The absorption of radiofrequency radiation is then measured. A typical spectrum is that of ethanol, CH<sub>3</sub>CH<sub>2</sub>OH, shown in Figure 9.1. The positions of the peaks can be read from the scale; always read to the centre of a multiplet. Many spectrometers print the peak position in Hz or δ, above the peak, which is very valuable when measuring coupling constants, but chemical shifts can be read from the scale. Note that the peaks are cut by flattened S-shaped curves; the height between the horizontal parts of the curve is proportional to the area enclosed by the peaks, which is itself proportional to the number of hydrogen atoms producing the peak. The area is also measured electronically, and recorded below the δ scale. Measurements of peak area are not precise, since they also include electronic noise and impurity peaks. They give the ratio of peak areas, which must be related to the hydrogen content of the sample. In this case, the ratio is 82.48 to 40.14 to 120.00, which in a molecule with six hydrogen atoms, makes the signals represent 2, 1 and 3 hydrogen atoms respectively.

The spectrum shown in Figure 9.1 consists of a quartet at δ3.71 representing two hydrogen atoms, a single peak at δ1.98 representing one hydrogen atom, and a triplet at δ1.24 representing three hydrogen atoms. Figure 9.2 shows that the peak at δ1.98 disappears after a D<sub>2</sub>O shake, so it is clearly the OH hydrogen. The CH<sub>2</sub> peak at δ3.71 is a quartet, so must be next to a CH<sub>3</sub> group, while the -CH<sub>3</sub> peak at δ1.24 is a triplet, so must be next to a CH<sub>2</sub> group. Clearly, the spectrum of ethanol can be assigned:



It is very important to note that the CH<sub>3</sub> group which absorbs at δ1.24 is a triplet because it is next to a CH<sub>2</sub>, and NOT because it has three hydrogen atoms on one carbon atom. The signal splitting depends on hydrogen atoms on NEIGHBOURING carbon atoms.

The next spectrum to consider is that of 1-methylethanol [propan-2-ol, (CH<sub>3</sub>)<sub>2</sub>CHOH], shown in Figure 9.3. The spectrum consists of a multiplet at δ4.02, a broad singlet at δ1.88, and a doublet at δ1.20. The peak at δ1.88 disappears on a D<sub>2</sub>O shake, so is clearly the OH peak. The doublet at δ1.20 represents six hydrogen atoms, whilst the multiplet at δ4.02 represents one hydrogen atom and is moved downfield by being next to an electronegative group, probably the hydroxyl. The doublet is from six hydrogen atoms on carbon atoms next to a carbon atom with one hydrogen atom. The multiplet at δ4.02 looks like a quintet, but since it is on a carbon atom next to carbons carrying six hydrogen atoms, it must be a septet. Deciding the exact multiplicity of multiplets of low intensity is often difficult, but an amplified expansion can help. The spectrum is clearly that of a molecule with a CH group attached to two CH<sub>3</sub> groups and an OH group:



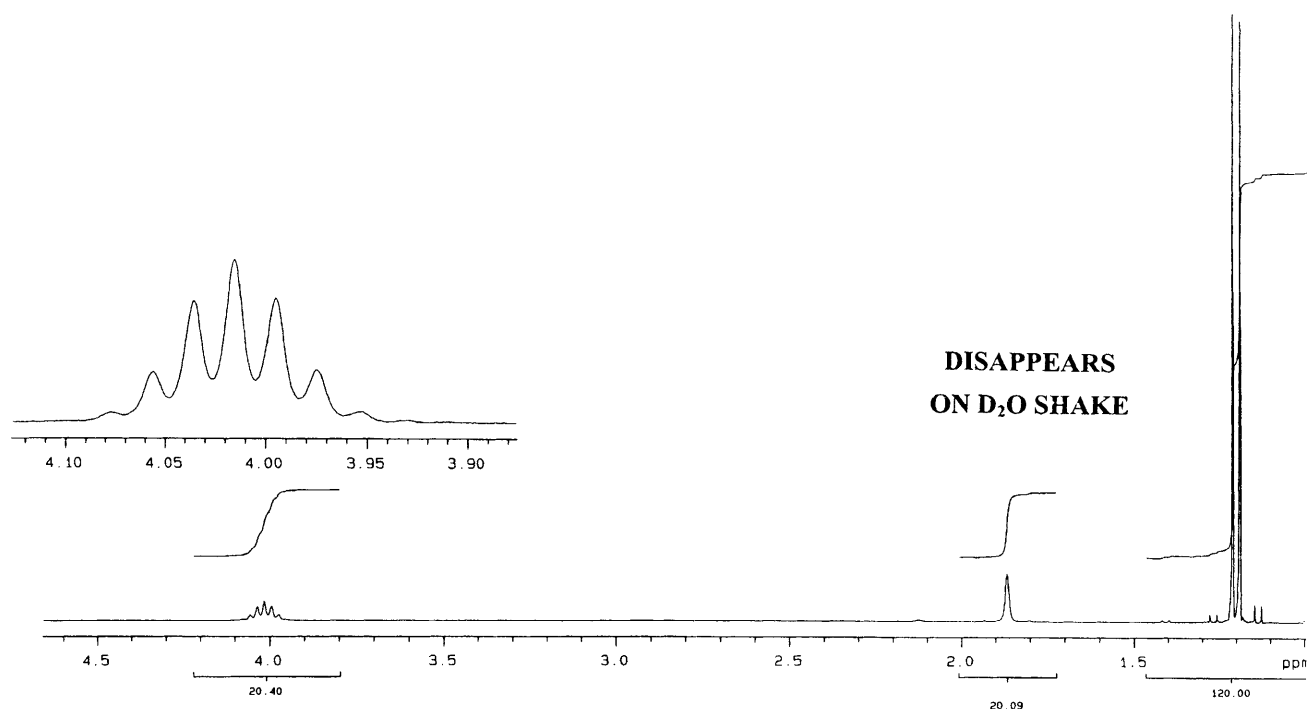


Figure 9.3

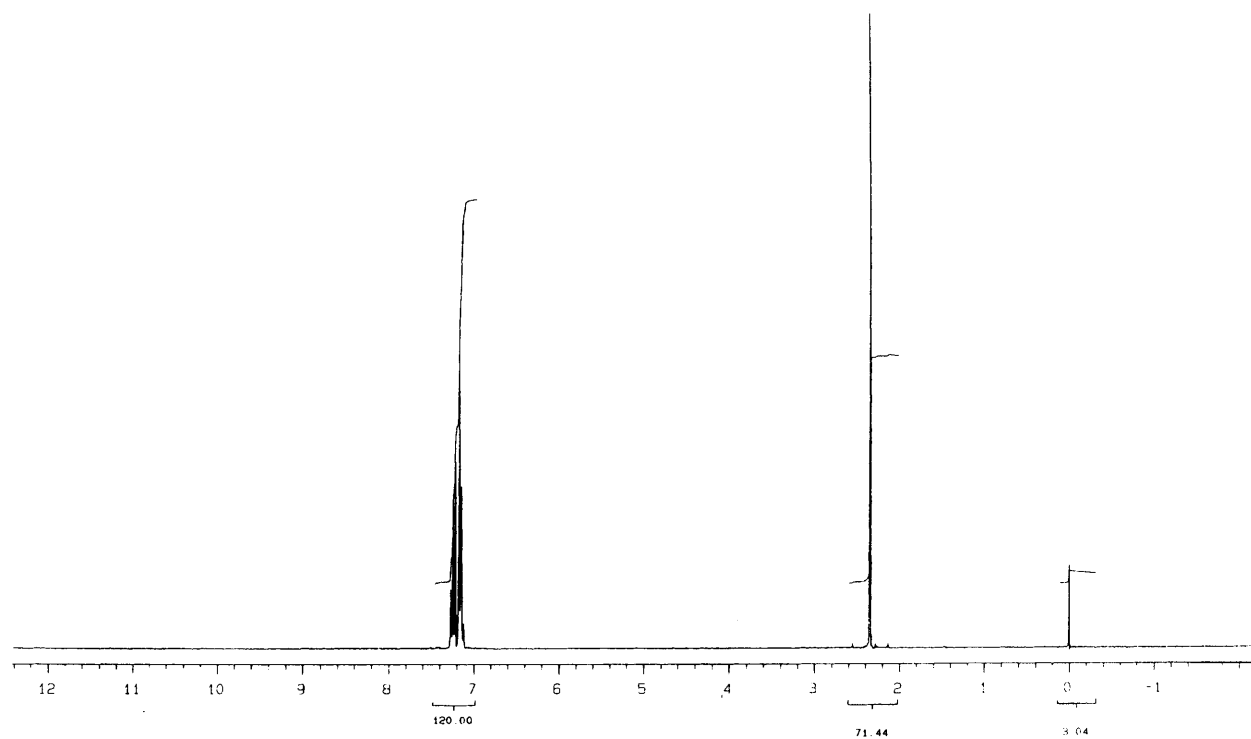


Figure 9.4

The next spectrum, shown in Figure 9.4, is that of toluene,  $\text{PhCH}_3$ . The singlet at  $\delta 2.35$  results from the methyl group, and is moved downfield from the previous methyl groups by the effect of the phenyl ring. The aromatic hydrogen atoms give rise to a complex multiplet around  $\delta 7.2$ . The chemical shifts of the aromatic hydrogen atoms depend on their distance from the  $\text{CH}_3$  group, and they split each other to give a complex system which we need not assign.

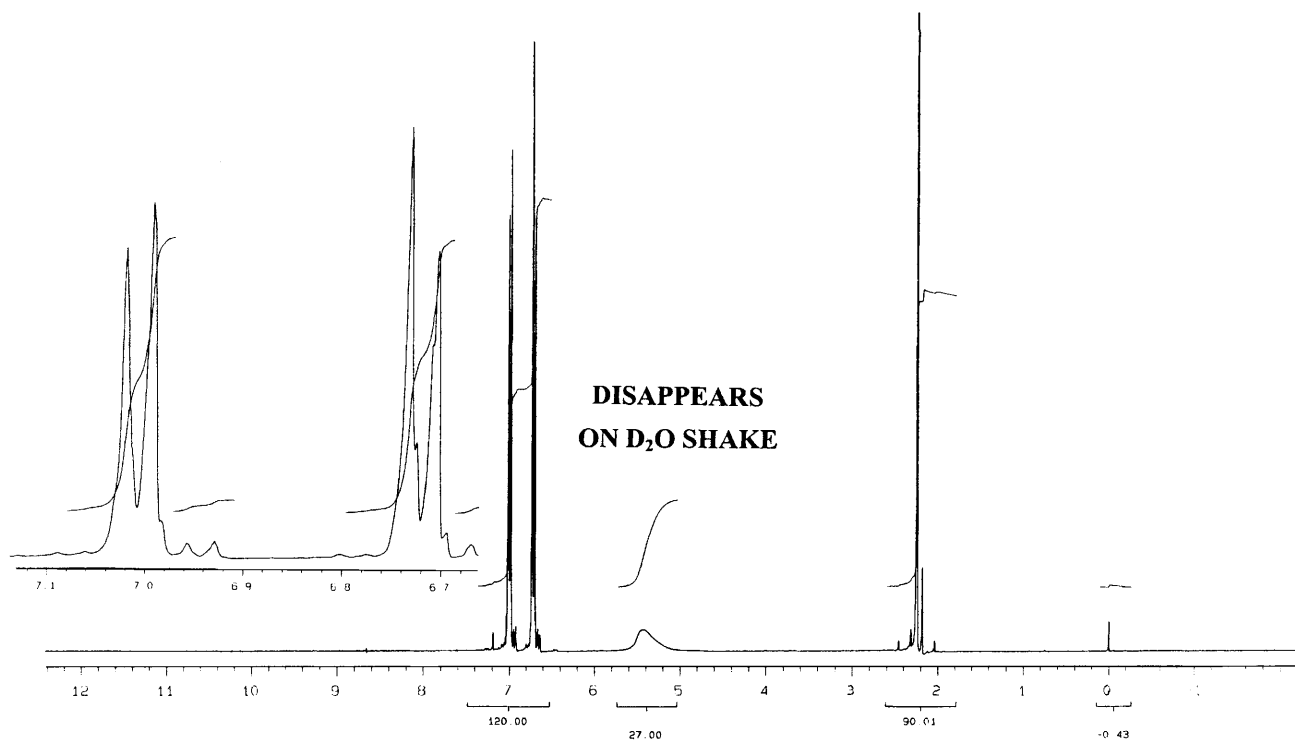


Figure 9.5

Despite the complexity of the aromatic region, we can often get useful information about the arrangement of substituents around the ring in disubstituted aromatic compounds by considering the symmetry, or lack of it, in the ring. Figure 9.5 shows the spectrum of a 1,4- or *para*-substituted compound, 4-methylphenol. The pattern of four peaks between  $\delta 6.7$  and  $7.1$  is typical of a *para*-substituted compound. The molecule has a plane of symmetry, so that the hydrogen atom on C-2 is coupled to the hydrogen atom on C-3, giving a pair of doublets identical to those produced by the hydrogen atoms on C-6 and C-5. The peak at  $\delta 5.4$  results from the phenolic OH, while the peak at  $\delta 2.25$  results from the methyl group. Small peaks near the main peak denote the presence of impurities. Figure 9.6 shows the spectrum of the 1,3- or *meta*-substituted isomer, 3-methylphenol. In a *meta*-substituted compound, the single hydrogen atom on the carbon atom between the substituents gives an unsplit peak, except for the small splittings arising from long range coupling. In this case, the peak from the C-2 hydrogen is at  $\delta 6.64$ . The spectrum of the 1,2- or *ortho*-substituted isomer, 2-methylphenol, is shown in Figure 9.7. In this case, two hydrogen atoms give doublets and two hydrogen atoms give triplets. The chemical shifts are often not enough to separate the peaks, and the result is frequently complex. If the substituents are identical, the spectra of all the disubstituted aromatics are greatly simplified.

Before we start to consider the interpretation of <sup>1</sup>H NMR spectra, two other spectra need to be considered, as they illustrate problems which are not readily predictable. The first of these is shown in Figure 9.8 and is the spectrum of 1,2-dimethoxyethane,  $\text{CH}_3\text{--O--CH}_2\text{--CH}_2\text{--O--CH}_3$ . It consists of two singlets, at  $\delta 3.37$  and  $\delta 3.51$ . The methyl peaks, at  $\delta 3.37$ , would not be expected to show any splitting, but the  $\text{CH}_2$  peaks, at  $\delta 3.51$ , are next to each other. However, it is always found that hydrogen atoms which are in identical environments do not split each other. We have no coupling, and hence no splitting of the  $\text{CH}_2$  groups which are in identical environments. The second spectrum is that shown in Figure 9.9, which is the spectrum of *N,N*-

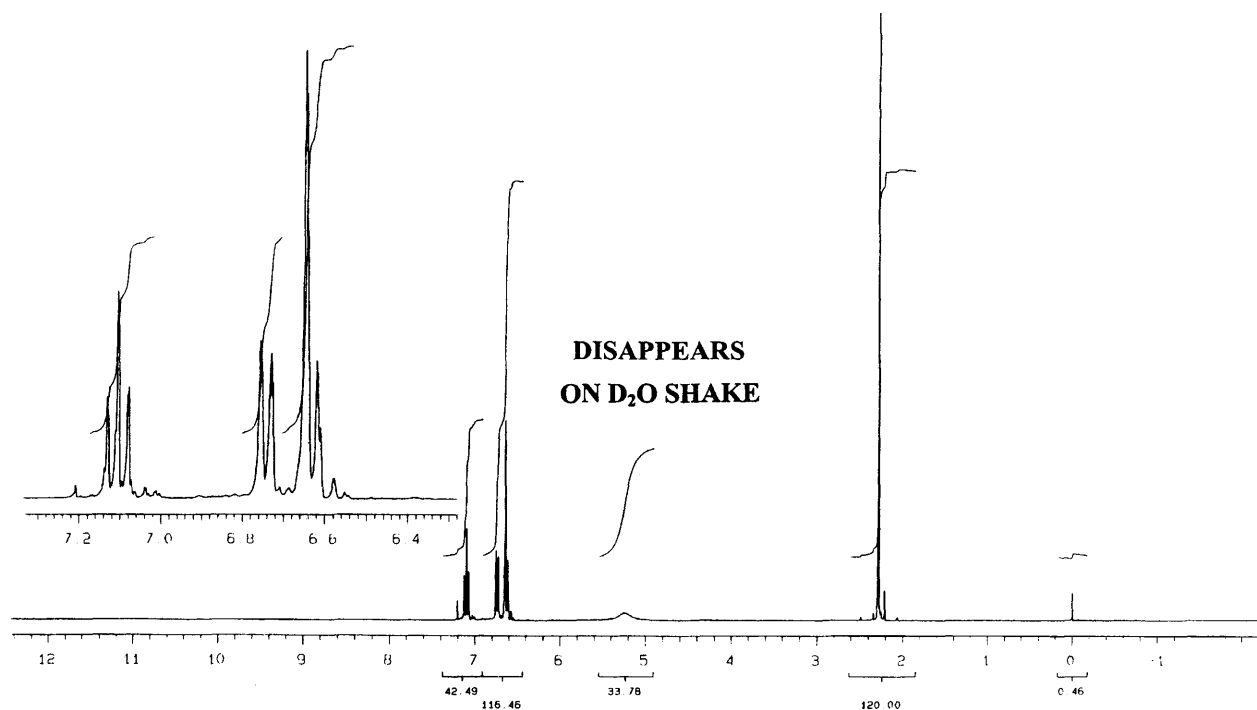


Figure 9.6

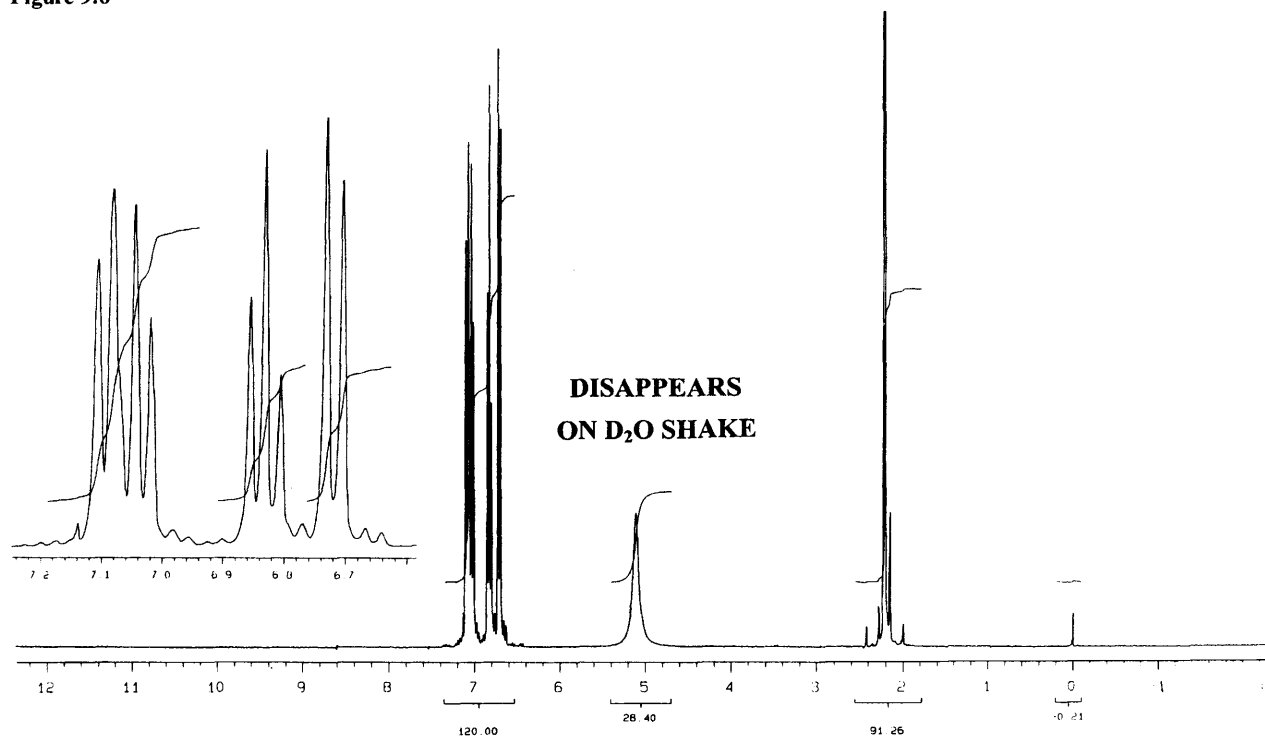
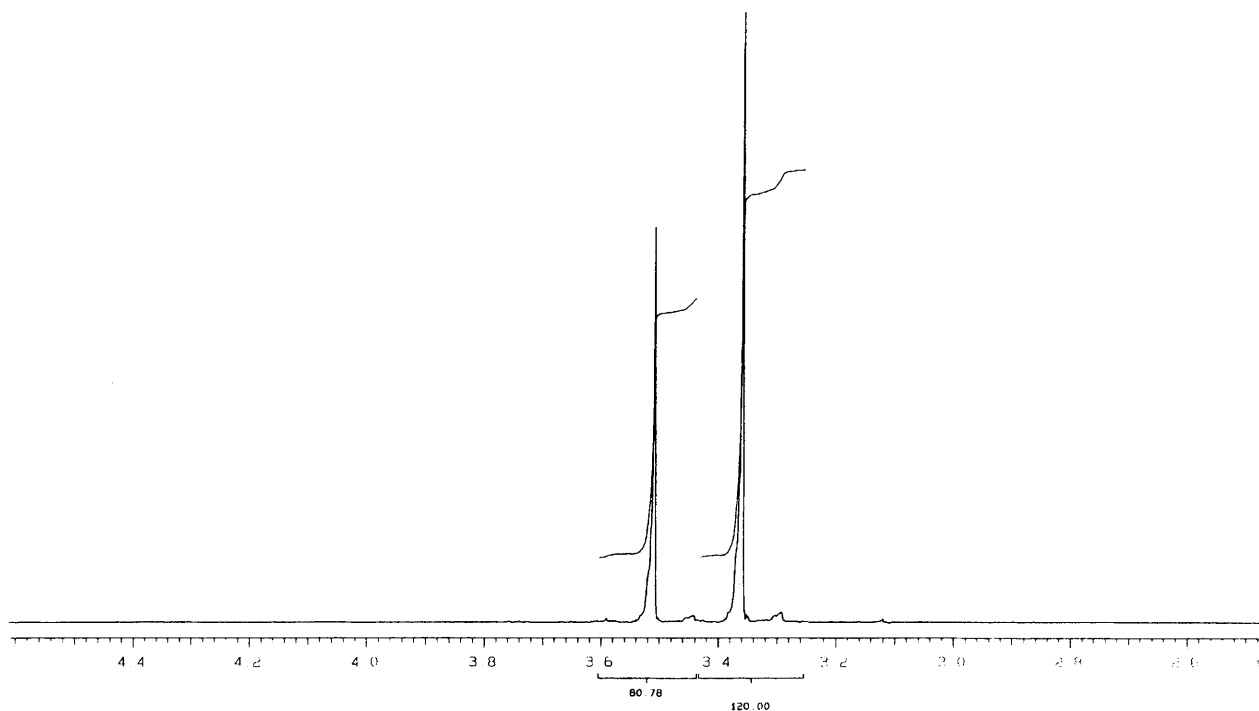
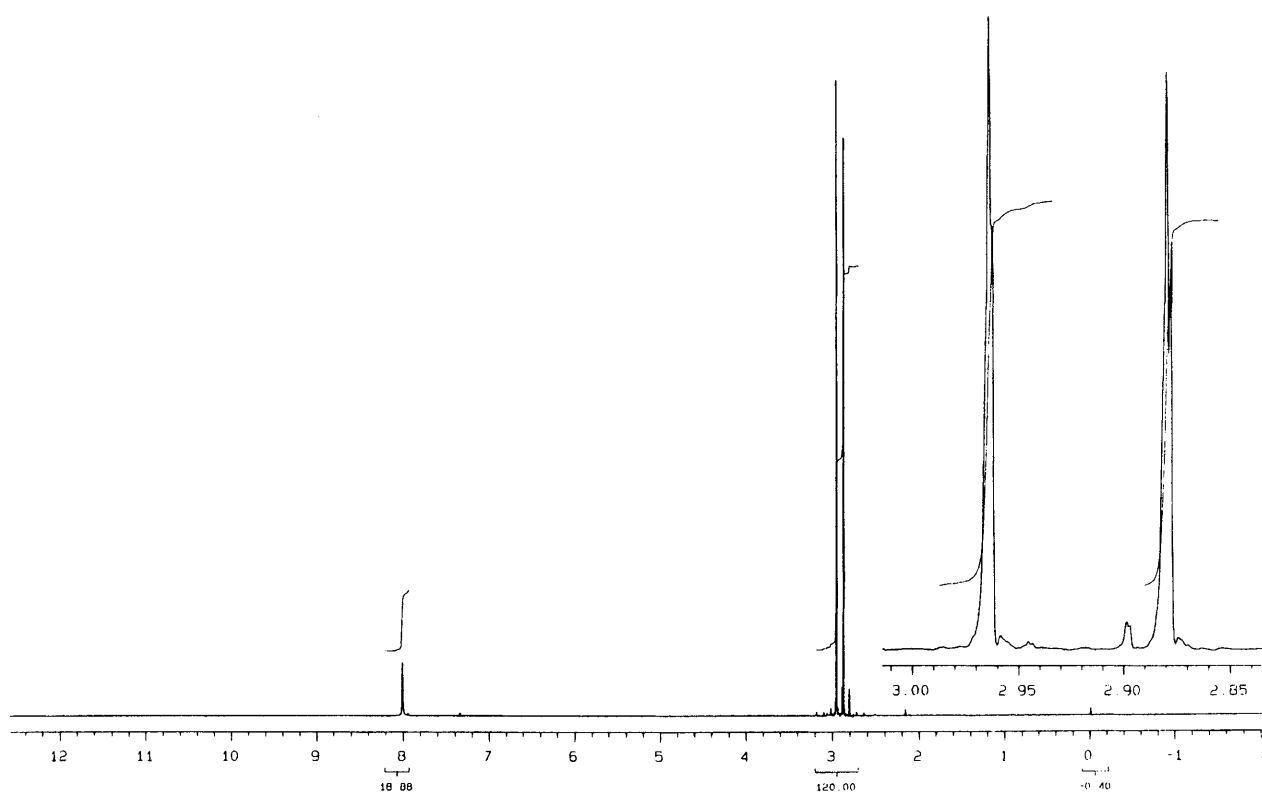


Figure 9.7

dimethylformamide,  $(\text{CH}_3)_2\text{NCHO}$ . The spectrum shows two signals at  $\delta 2.88$  and  $\delta 2.96$ , which at first glance might be thought to be a  $\text{CH}_3$  group next to a  $\text{CH}$ . However, we do not have any multiplets in the spectrum, so that separation of the signals cannot be the result of splitting, and must result from chemical shift. Although both methyl groups are attached to the same nitrogen atom, there is restricted rotation around the  $\text{N}-\text{C}$  bond, and the two methyl groups are in different positions relative to the carbonyl group, and hence have different chemical shifts.

**Figure 9.8****Figure 9.9**

We can now look at unknown spectra. The first of these, shown in Figure 9.10, is of a substance  $\text{C}_4\text{H}_8\text{O}_2$ . When we look at the spectrum, we can see that it consists of a quartet at  $\delta 4.12$ , a singlet at  $\delta 2.05$  and a triplet at  $\delta 1.27$ . The peaks all show very small extra splittings, due to long range coupling, which in this case are unimportant. The three groups of peaks have peak areas in the

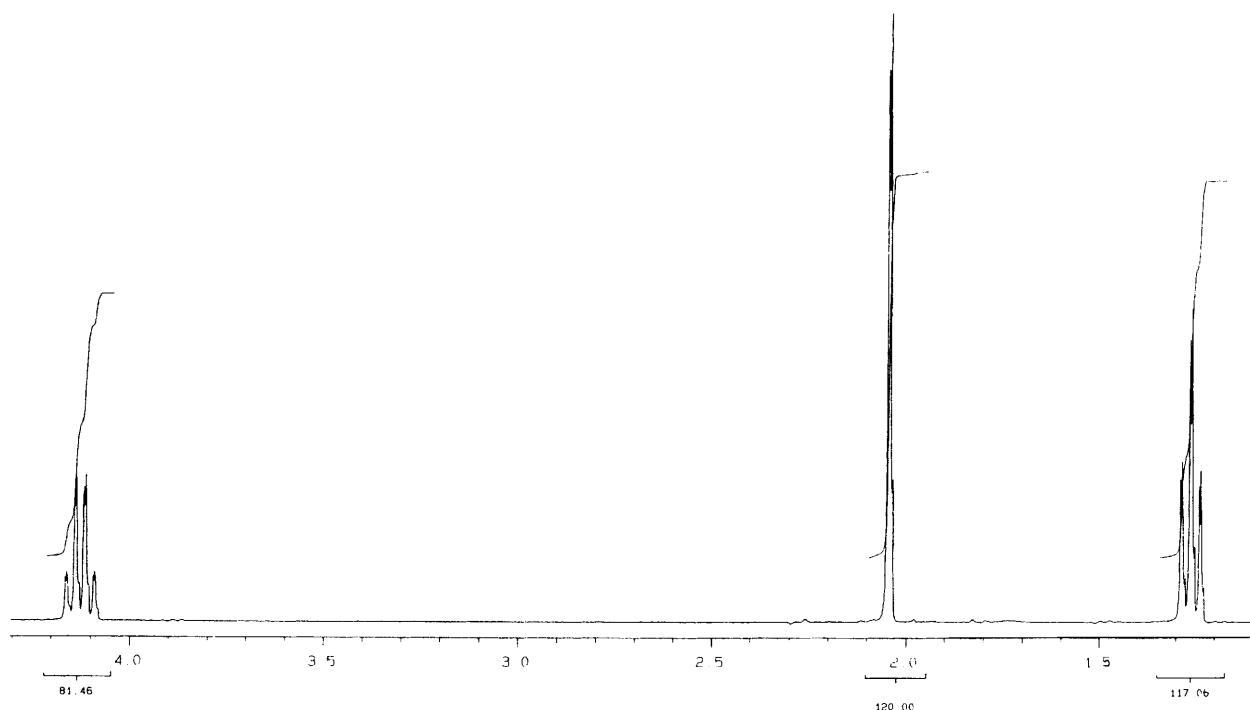
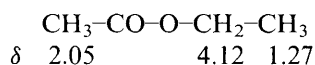


Figure 9.10

ratio 81.46 to 120.00 to 117.06, which is approximately 2 : 3 : 3. Since we have eight hydrogen atoms in the molecule, we must have a  $\text{CH}_2$  group absorbing at  $\delta$  4.12, a  $\text{CH}_3$  group at  $\delta$  2.05 and another  $\text{CH}_3$  group at  $\delta$  1.27. The chemical shifts show that the hydrogen atoms giving the peak at  $\delta$  4.12 are probably next to a strongly electronegative group, and the hydrogen atoms giving the peak at  $\delta$  2.05 are next to a weaker electronegative group or further away from a strongly electronegative group. The  $\text{CH}_2$  group giving rise to the quartet at  $\delta$  4.12 must be next to a  $\text{CH}_3$  group, and the  $\text{CH}_3$  group giving rise to the triplet at  $\delta$  1.27 must be next to a  $\text{CH}_2$  group. Clearly, these form an ethyl group, attached to an electronegative atom or group. The  $\text{CH}_3$  group giving rise to the peak at  $\delta$  2.05 is not next to a hydrogen bearing carbon atom. We must now look at the original molecular formula,  $\text{C}_4\text{H}_8\text{O}_2$ . We have accounted for  $\text{C}_2\text{H}_5$  plus  $\text{CH}_3$ , so we have  $\text{COO}$  unaccounted for. This is most likely to be an ester group. Since the  $\text{CH}_2$  of the ethyl group is moved down to  $\delta$  4.12, it must be attached to the oxygen atom. The unsplit methyl group at  $\delta$  2.05 must be attached to the carbonyl group, which moves it a shorter distance downfield. The substance is thus ethyl acetate:



The next substance, whose  $^1\text{H}$  NMR spectrum is shown in Figure 9.11, has the molecular formula  $\text{C}_4\text{H}_9\text{Br}$ . The spectrum shows four groups of peaks, plus added TMS at  $\delta$  0. The groups of peaks are at  $\delta$  3.41, 1.85, 1.47 and 0.94, in the ratio 83.15 to 81.47 to 84.01 to 120.00, which is approximately 2:2:2:3. Combining this data with the molecular formula, we have three  $\text{CH}_2$  groups and a  $\text{CH}_3$  group. The  $\text{CH}_2$  group absorbing at  $\delta$  3.41 is probably downfield because it is attached to the bromine atom. Thus, we have now accounted for all the atoms listed in the molecular formula. Next, we must consider the splitting patterns. The peaks at  $\delta$  3.41 form a triplet, those at  $\delta$  1.85 a quintet.



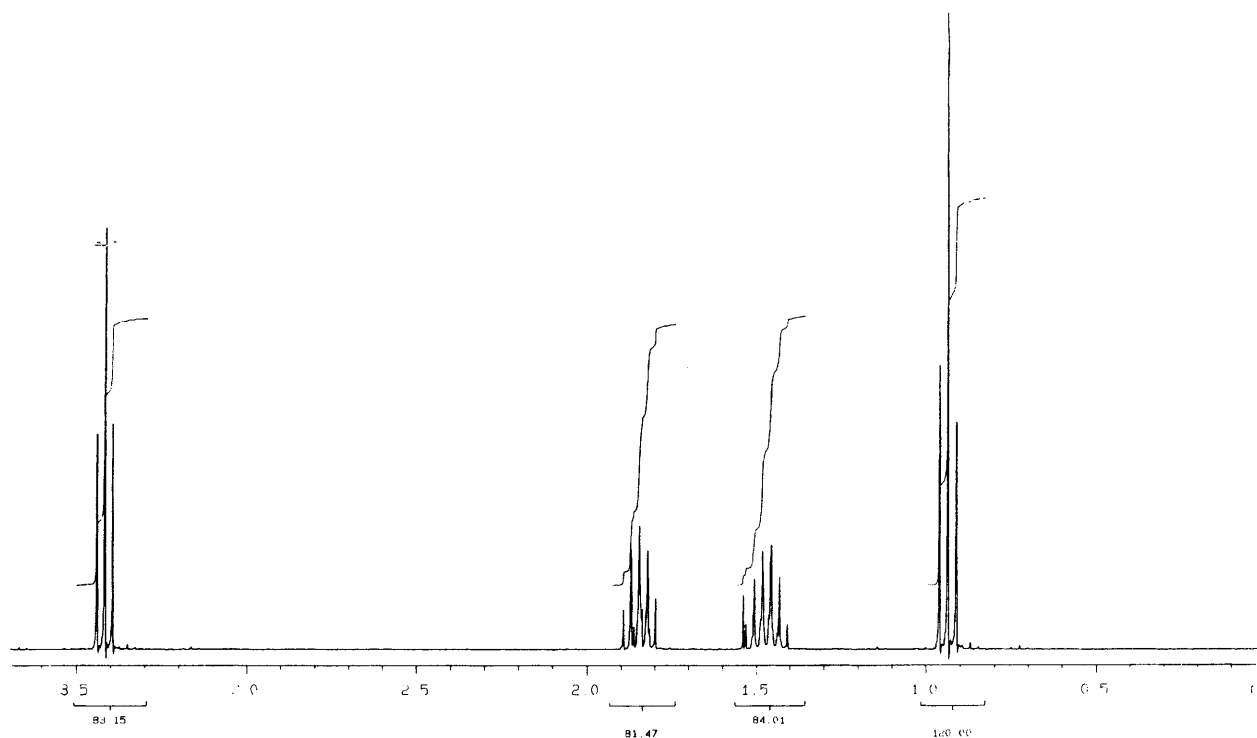


Figure 9.11

At  $\delta 1.47$  we have a symmetrical sextet, with a small extra peak at  $\delta 1.54$ . Since this does not fit with an otherwise symmetrical group, and is far too small to represent even a single hydrogen, it is probably an impurity. At  $\delta 0.94$ , we have a triplet. It is often convenient to summarise the data:

Peak at $\delta$	No. of H	Next to
3.41	2	2H
1.85	2	4H
1.47	2	5H
0.94	3	2H

We next seek to assemble the groups into a molecule. We can do this by using the diminishing effect on chemical shift of the bromine atom, or we can use the splitting patterns. We have two 'end of chain' groups,  $\text{CH}_2\text{Br}$  and  $\text{CH}_3$ , so we have a straight chain molecule. Assembly can start at either end of the chain. Starting from  $\text{CH}_2\text{Br}$ , at  $\delta 3.41$ , we see that it is a triplet, so must be next to a  $\text{CH}_2$ . We have two further  $\text{CH}_2$  groups, one a quintet, the other a sextet. If we put the latter next to our  $\text{CH}_2\text{Br}$ , then it would also have to have a  $\text{CH}_3$  group attached, giving  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ , which would leave us with an unused  $\text{CH}_2$  group. However, if we join the  $\text{CH}_2$  group which absorbs at  $\delta 1.85$ , to our  $\text{CH}_2\text{Br}$ , then it would have to be attached to another  $\text{CH}_2$ , since it is next to carbon atoms carrying four hydrogens. This has to be the only remaining  $\text{CH}_2$ , which absorbs at  $\delta 1.47$ , and since it has to be next to carbon atoms carrying a total of five hydrogens, must be next to the only group left, the  $\text{CH}_3$ .

If we started at the other end of the chain, with the  $\text{CH}_3$  group, then this must be next to a  $\text{CH}_2$ . If it were attached to the  $\text{CH}_2$  which gives a quintet at  $\delta 1.85$ , then the next group along the chain would have to be a  $\text{CH}$  group,

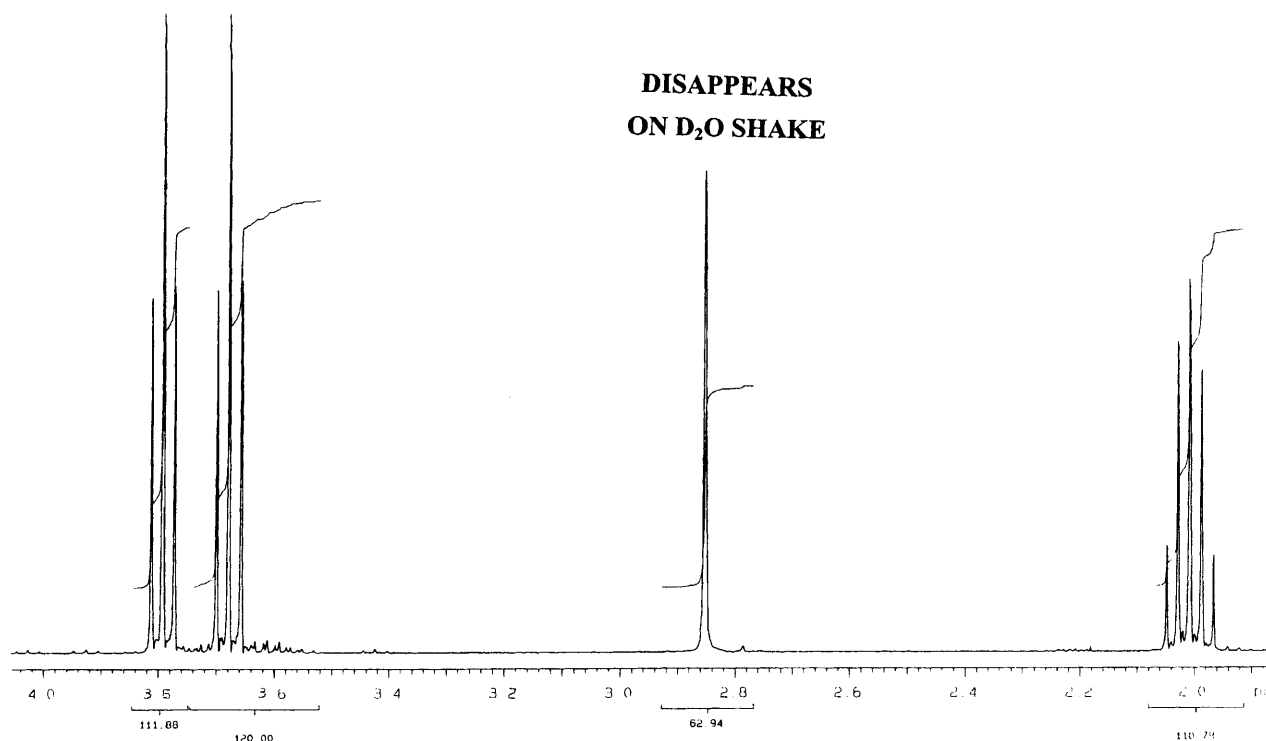


Figure 9.12

which we do not have. It must therefore be attached to the  $\text{CH}_2$  group which gives a sextet at  $\delta 1.47$ , which must be next to another  $\text{CH}_2$ , clearly that absorbing at  $\delta 1.85$ . This needs to be attached to another  $\text{CH}_2$ , clearly the chain ending group at  $\delta 3.41$ . Either approach gives us:

	$\text{Br}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$			
$\delta$	3.41	1.85	1.47	0.94
next to	2H	4H	5H	2H

Our assignment fits with the expected decrease in chemical shift as we move away from the electronegative bromine.

The next spectrum, shown in Figure 9.12, is of a substance  $\text{C}_3\text{H}_7\text{OCl}$ . The spectrum consists of peaks at  $\delta 3.79$  (2H, triplet),  $3.68$  (2H, triplet),  $2.85$  (1H, singlet) and  $2.01$  (2H, quintet). The peak at  $\delta 2.85$  disappears on shaking the sample with  $\text{D}_2\text{O}$ , so the hydrogen is probably attached to the oxygen atom. Thus we have

Peak at $\delta$	No. of H	Next to
3.79	2	2H
3.68	2	2H
2.01	2	4H

The peaks at  $\delta 3.79$  and  $3.68$  are moved downfield, by the electronegative OH and Cl respectively. The molecule thus consists of three  $\text{CH}_2$  groups, so that the middle  $\text{CH}_2$  is a quintet, while the outer  $\text{CH}_2$  groups have a chlorine attached to one, and a hydroxyl attached to the other:

	$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$			
$\delta$	3.68	2.01	3.79	2.85
next to	2H	4H	2H	

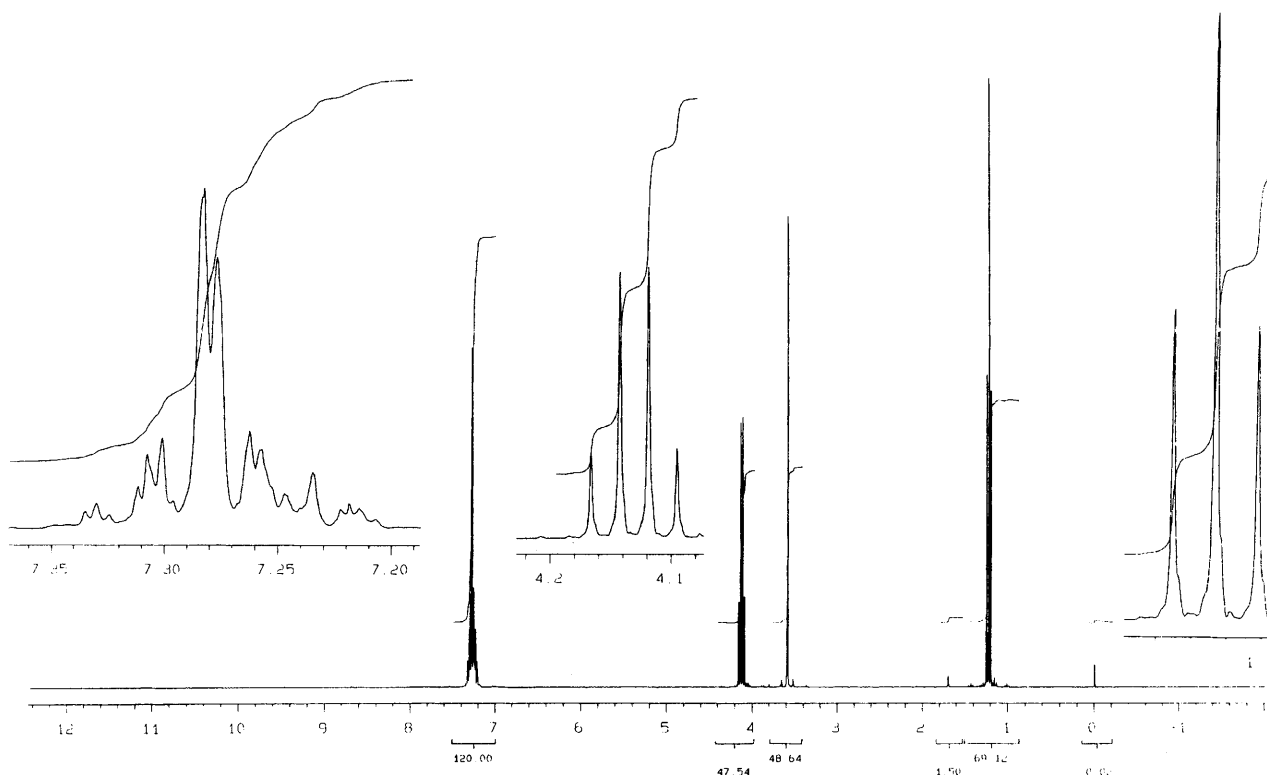
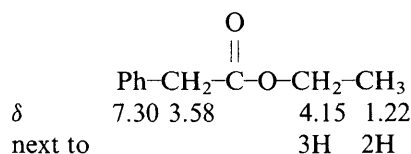


Figure 9.13

The next spectrum, shown in Figure 9.13, is of a substance  $\text{C}_{10}\text{H}_{12}\text{O}_2$ . Parts of the spectrum have been enlarged to help interpretation. The spectrum shows peaks at  $\delta 7.30$  (5H, complex multiplet), 4.15 (2H, quartet), 3.58 (2H, singlet) and 1.22 (3H, triplet). Thus, we have

Peak at $\delta$	No. of H	Next to
7.30	5	—
4.15	2	3H
3.58	2	Zero H
1.22	3	2H

The multiplet at  $\delta 7.30$  is clearly from an aromatic ring. It represents 5H, so the ring must be monosubstituted. The peaks at  $\delta 4.15$  and 1.22 represent an ethyl group next to an electronegative atom, and the peak at  $\delta 3.58$  a  $\text{CH}_2$ , which has no hydrogen atoms on neighbouring carbon atoms, is next to one or two electronegative groups. These groups,  $\text{C}_6\text{H}_5$  plus  $\text{C}_2\text{H}_5$  plus  $\text{CH}_2$ , account for  $\text{C}_9\text{H}_{12}$  of the  $\text{C}_{10}\text{H}_{12}\text{O}_2$  of the original substance, so we have  $\text{CO}_2$  left over; this is probably an ester linkage. The ethyl group must be attached to the oxygen atom of the ester, so that the  $\text{CH}_2$  links the carbonyl group to the chain ending phenyl group:



The final example has the spectrum shown in Figure 9.14, and has the molecular formula  $\text{C}_5\text{H}_{10}\text{O}$ . The spectrum shows peaks at  $\delta 5.40$  (1H, broad

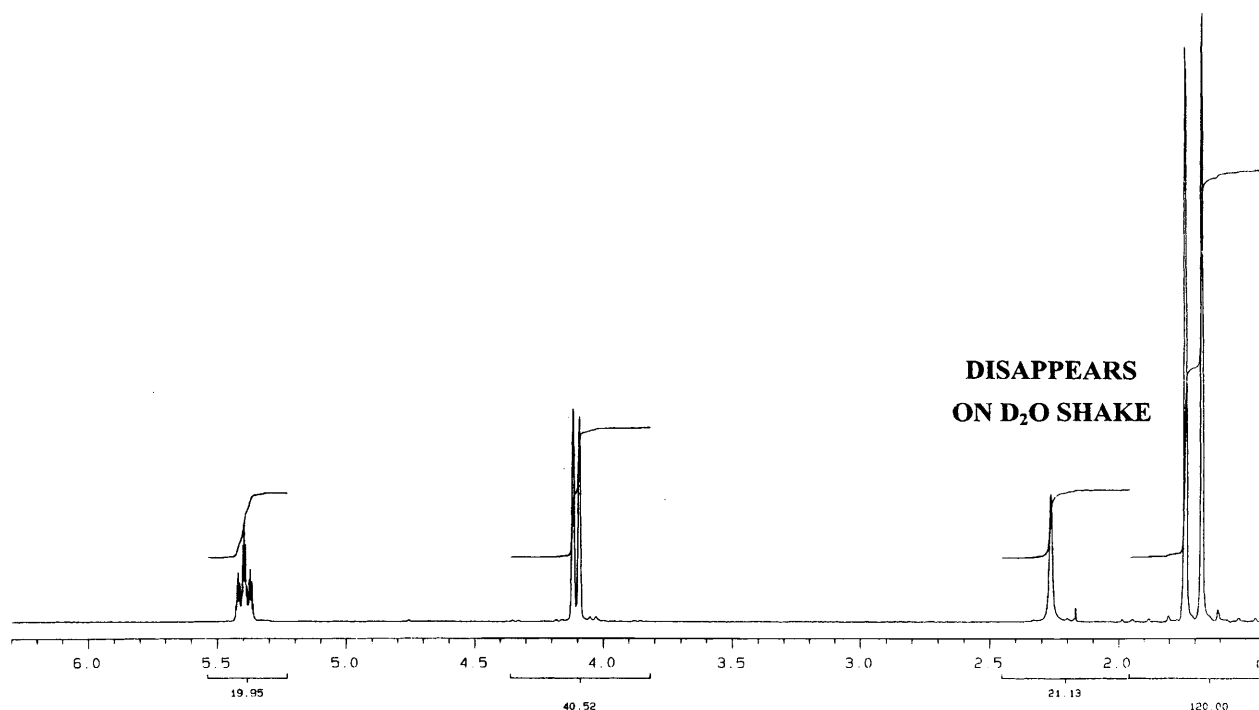
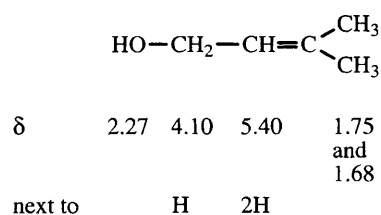


Figure 9.14

triplet), 4.10 (2H, doublet), 2.27 (1H, singlet), 1.75 (3H, singlet) and 1.68 (3H, singlet). We know that the peaks at  $\delta$ 1.75 and 1.68 are separate peaks, rather than a single split peak, because their separation comfortably exceeds any other splitting in the spectrum. It is an unbreakable rule of  $^1\text{H}$  NMR spectroscopy that if  $\text{H}_\text{A}$  splits  $\text{H}_\text{B}$ , then  $\text{H}_\text{B}$  splits  $\text{H}_\text{A}$ , and the splittings are the same size. The peak at  $\delta$ 5.40 (1H) probably results from an H atom attached to a  $\text{C}=\text{C}$  double bond. The peak at  $\delta$ 2.27 disappears on a  $\text{D}_2\text{O}$  shake, so the hydrogen is attached to the oxygen in the molecule, and this OH is probably responsible for the downfield shift of the  $\text{CH}_2$  group to  $\delta$ 4.10. We thus have:

Peak at $\delta$	No. of H	Next to
5.40	1	2H
4.10	2	1H
1.75	3	—
1.68	3	—

The molecule must consist of a double bond to which H,  $\text{CH}_2\text{OH}$ ,  $\text{CH}_3$  and  $\text{CH}_3$  are all attached. However, the splitting between the peaks at  $\delta$ 5.40 and 4.10 suggests they are on neighbouring carbon atoms, so the structure must be:



The extra line broadening on the peaks at  $\delta$ 5.40 probably results from a long range interaction with the methyl groups. Note that when we encountered the

<sup>13</sup>C NMR spectrum of this molecule in Chapter 5, we were unable to prove the structure. Interaction between hydrogen atoms on neighbouring carbon atoms now shows us which carbon atom is joined to which.

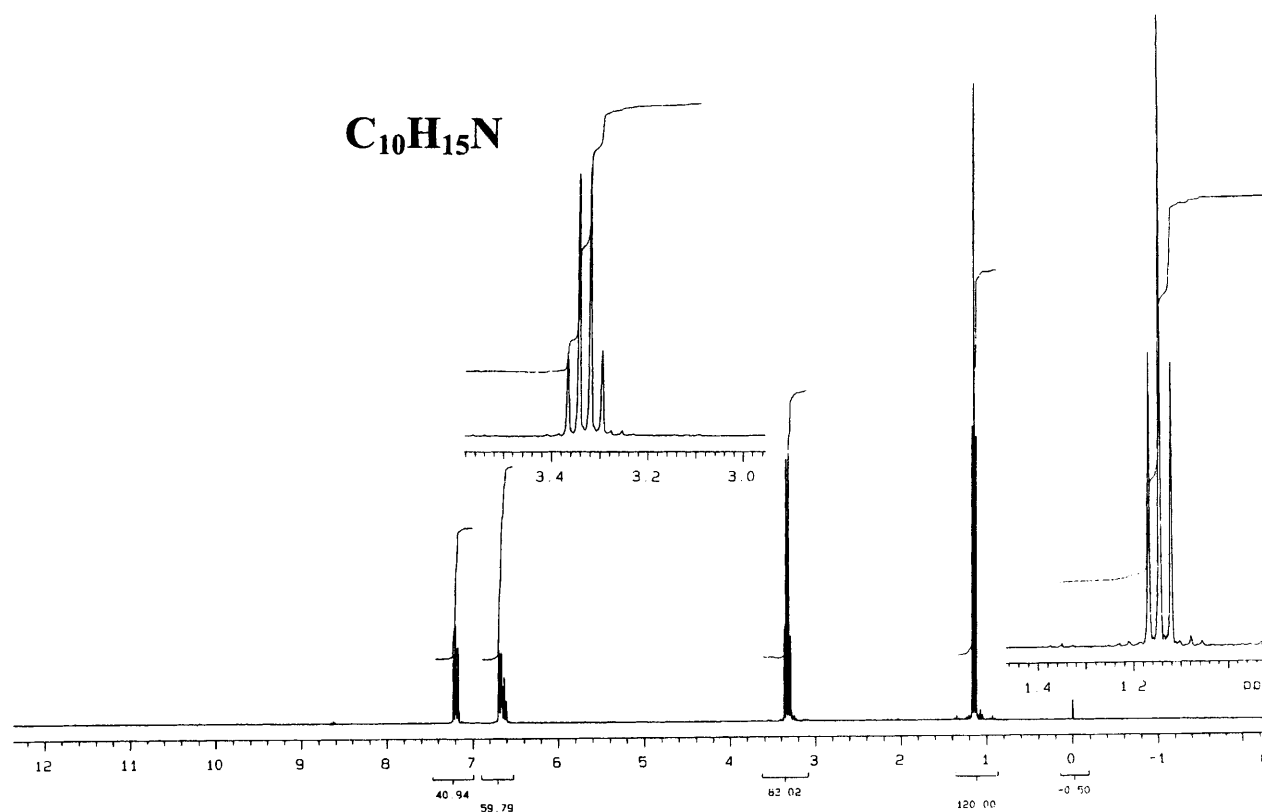
### Summary

To determine a structure from a <sup>1</sup>H NMR spectrum, we usually need the molecular formula. Analysis of the spectrum involves:

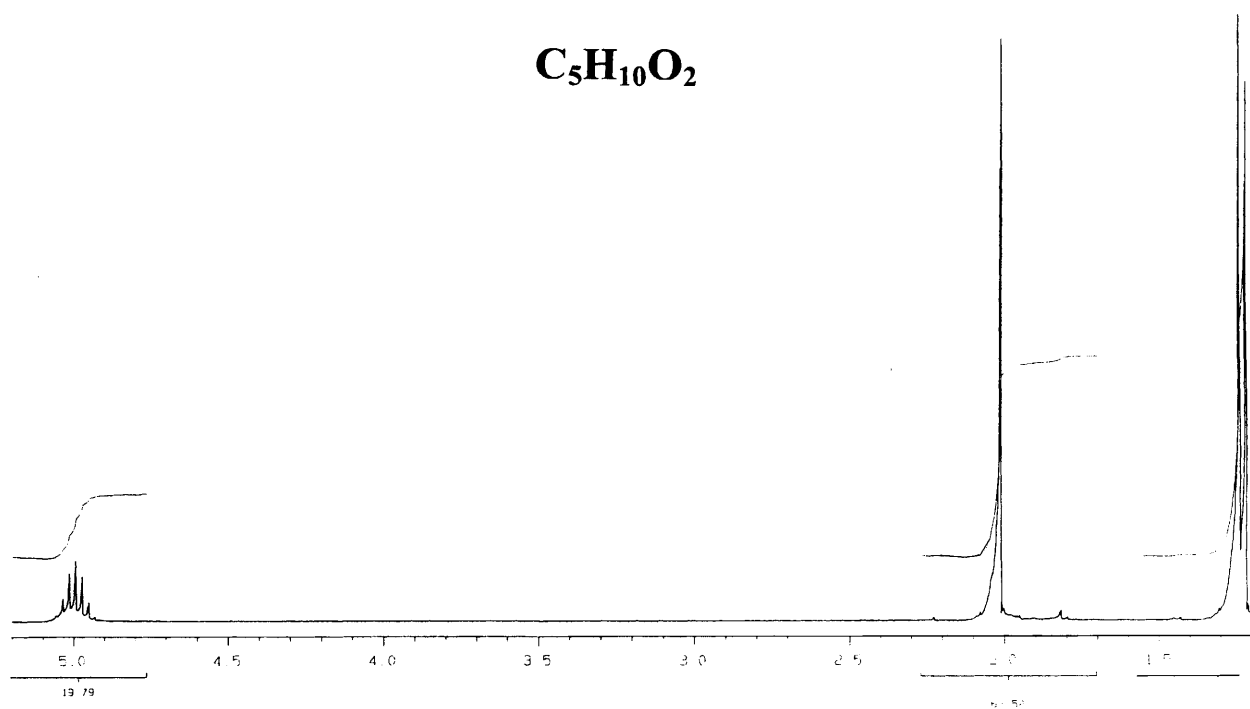
- A. Look at the integration, and from the molecular formula see how many hydrogen atoms are represented by each group of signals.
- B. Look for any signals which disappear on a D<sub>2</sub>O shake.
- C. See how many carbon atoms are involved in the groups of hydrogen atoms. Then look at the molecular formula to see how many carbon atoms are left over, and which other atoms the molecule contains.
- D. Look at the chemical shifts. This should identify alkenes, alkynes and aromatic groups, and show which atoms are moved downfield by neighbouring electronegative substituents.
- E. Look at the splittings of the peaks, and hence determine how many hydrogen atoms are on the carbon next to that carrying the hydrogen atom(s) that you are studying.
- F. Assemble the atoms into a molecule. With short carbon chains, it will be obvious how the carbon atoms fit together, but for longer chains, work from a 'chain ending group' (*i.e.* a group with only one unused linkage), such as CH<sub>3</sub>, CH<sub>2</sub>OH, CH<sub>2</sub>Br, =CH<sub>2</sub>, phenyl, *etc.* If you have more than two of these groups, the molecule must be branched.

### Problems in interpreting <sup>1</sup>H NMR spectra

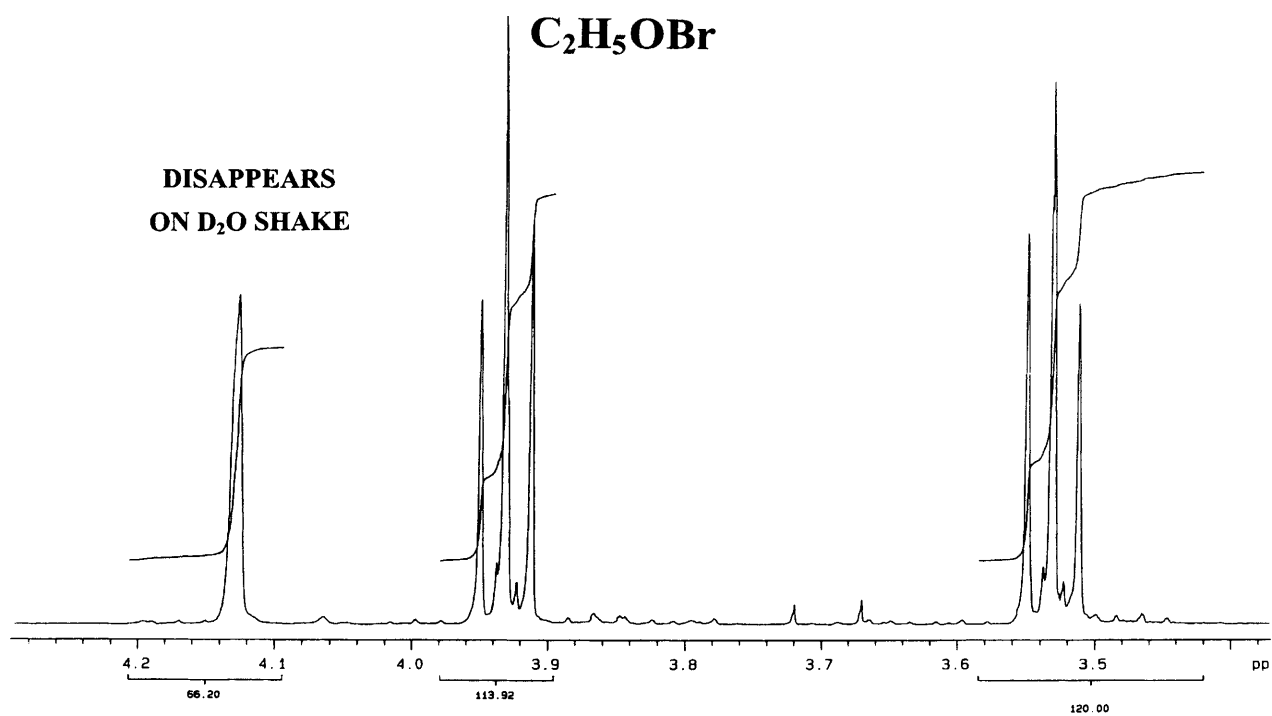
You are given the <sup>1</sup>H NMR spectra and molecular formulae of 10 substances. Assign all the structures from the data.



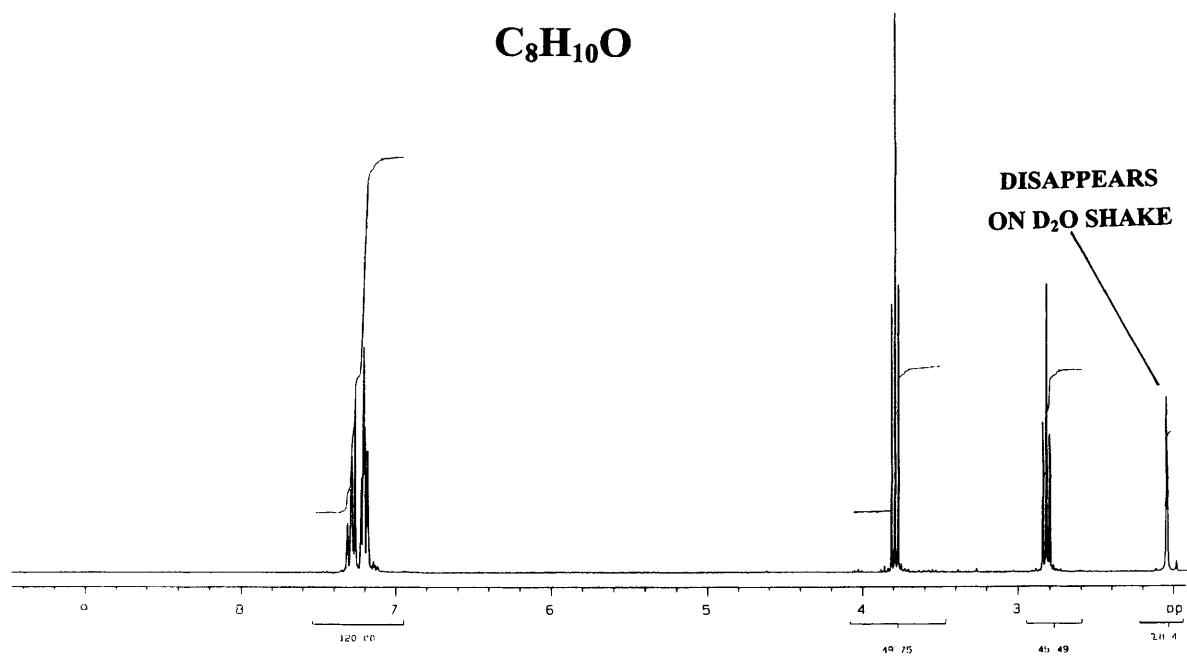
Sample 9.1



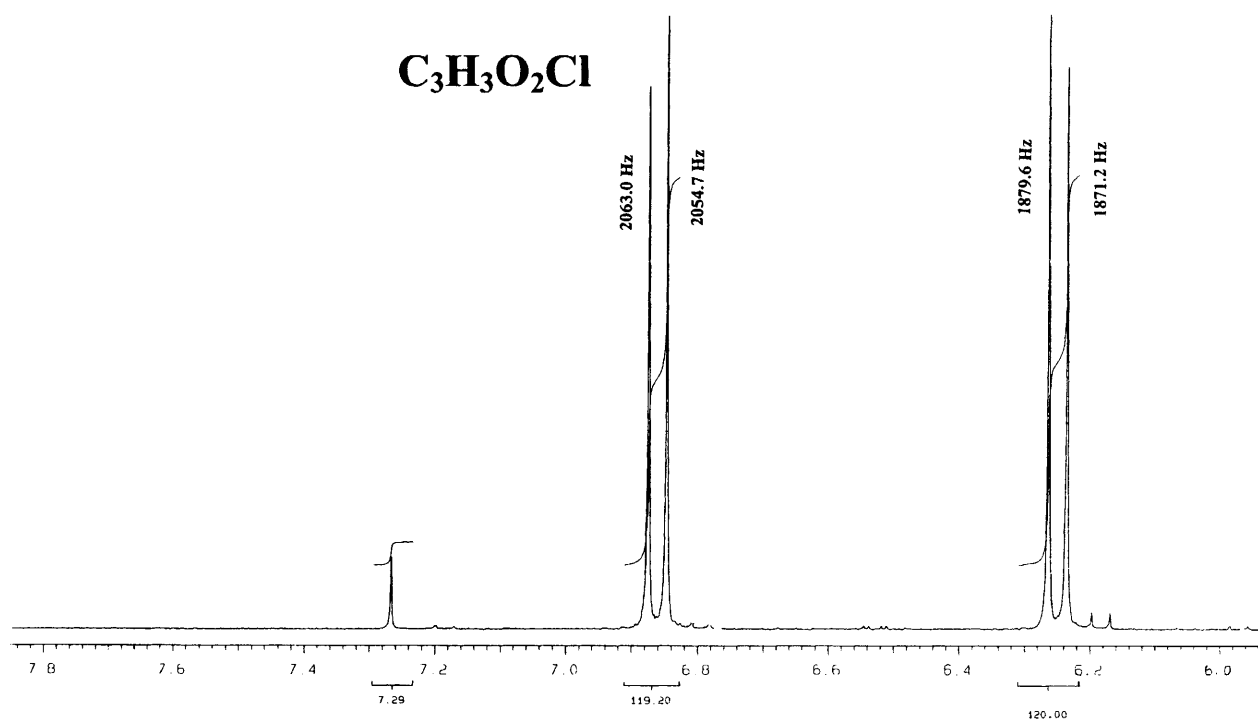
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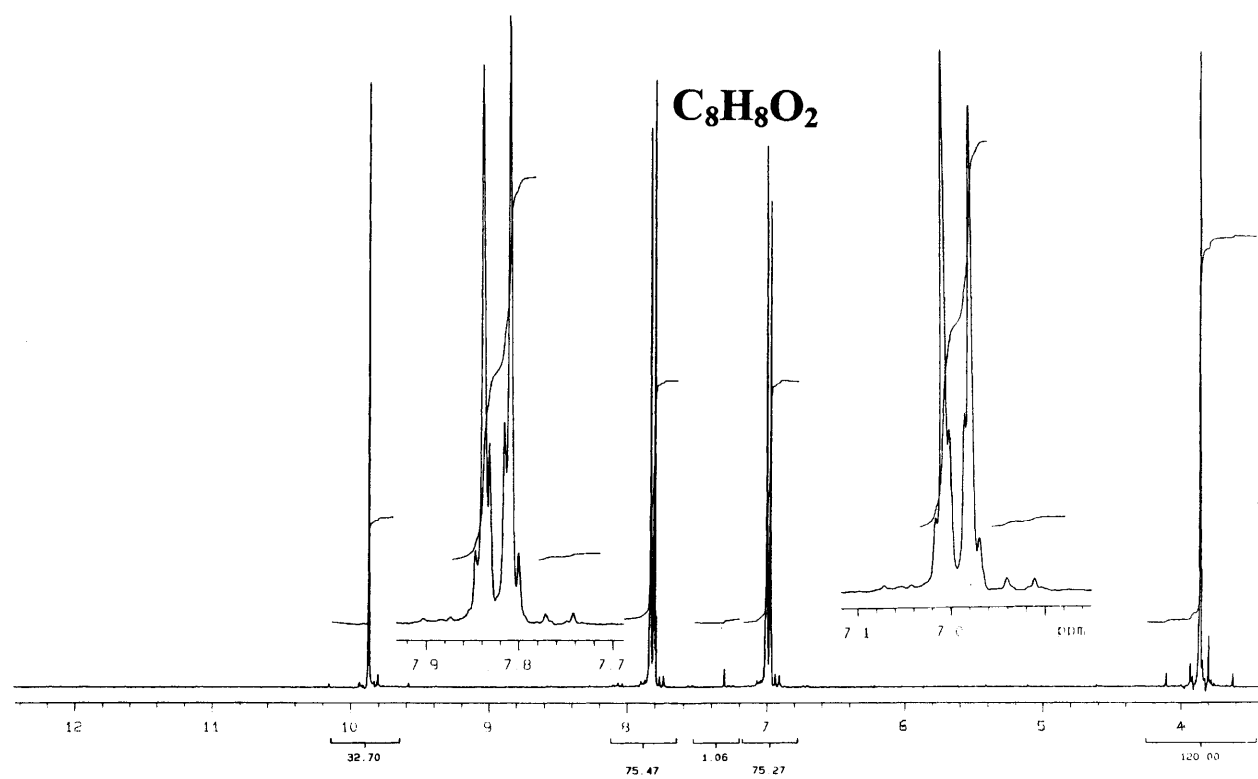
Sample 9.3



Sample 9.4

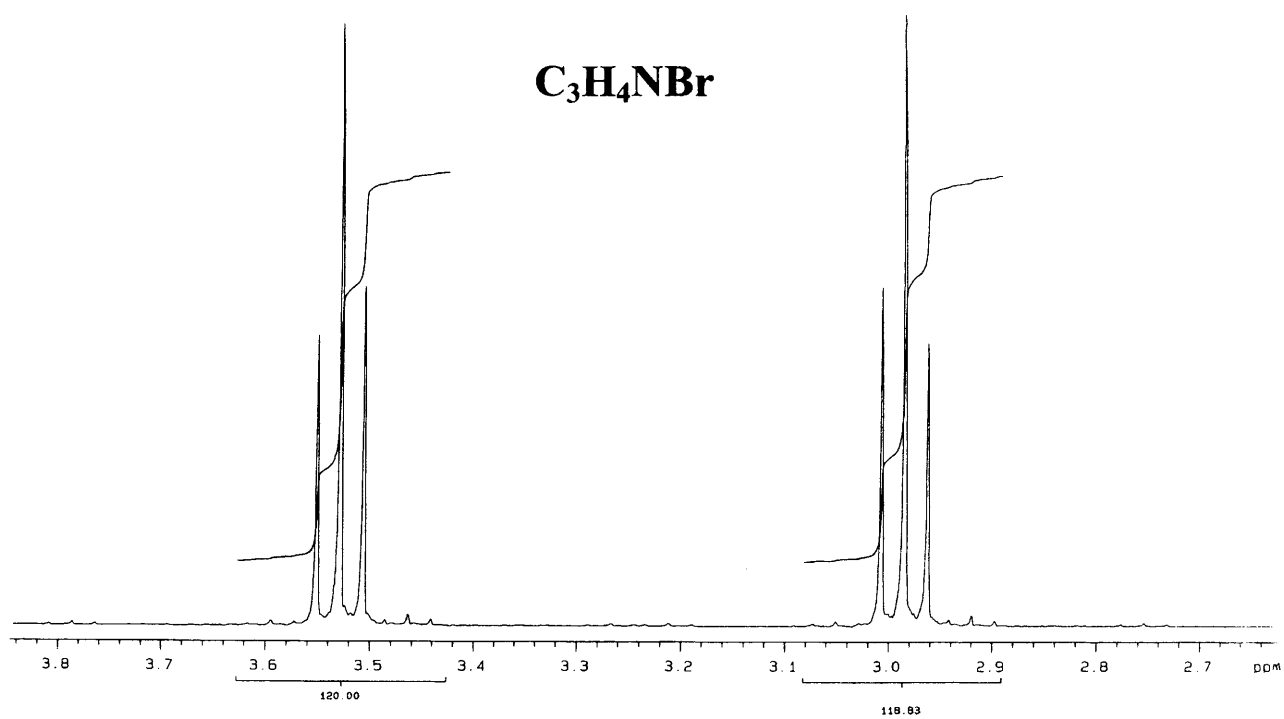


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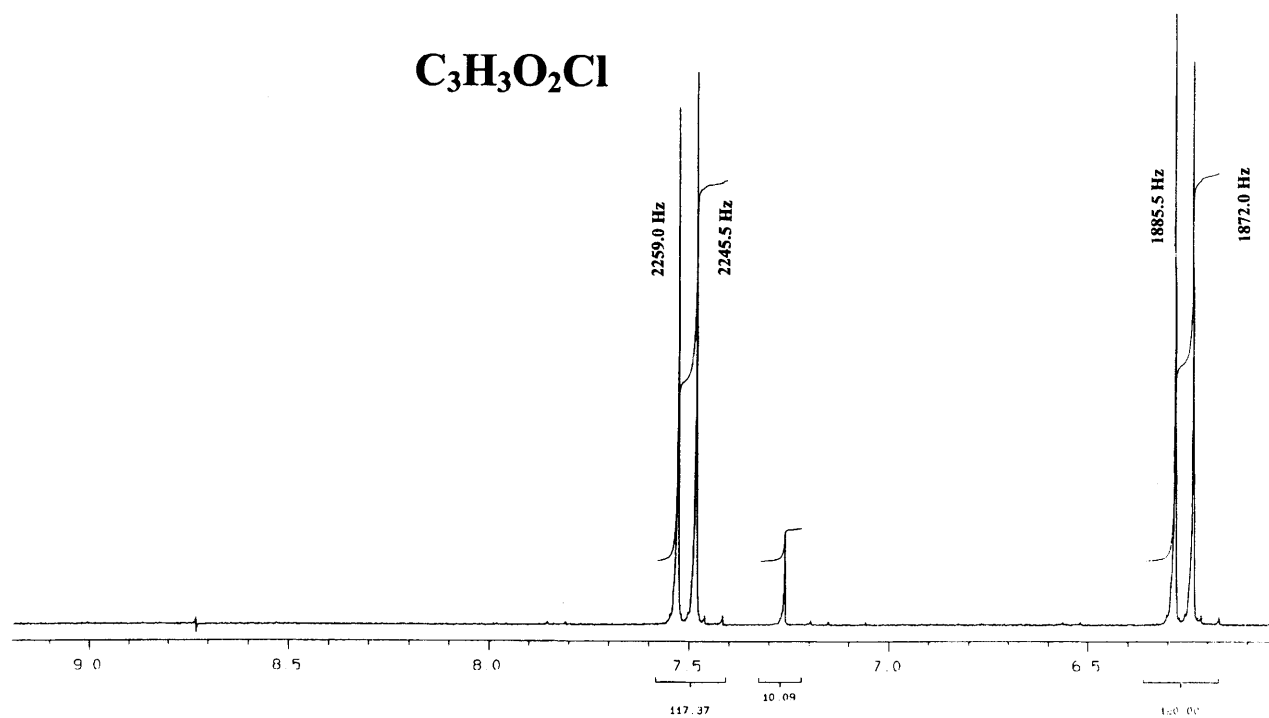


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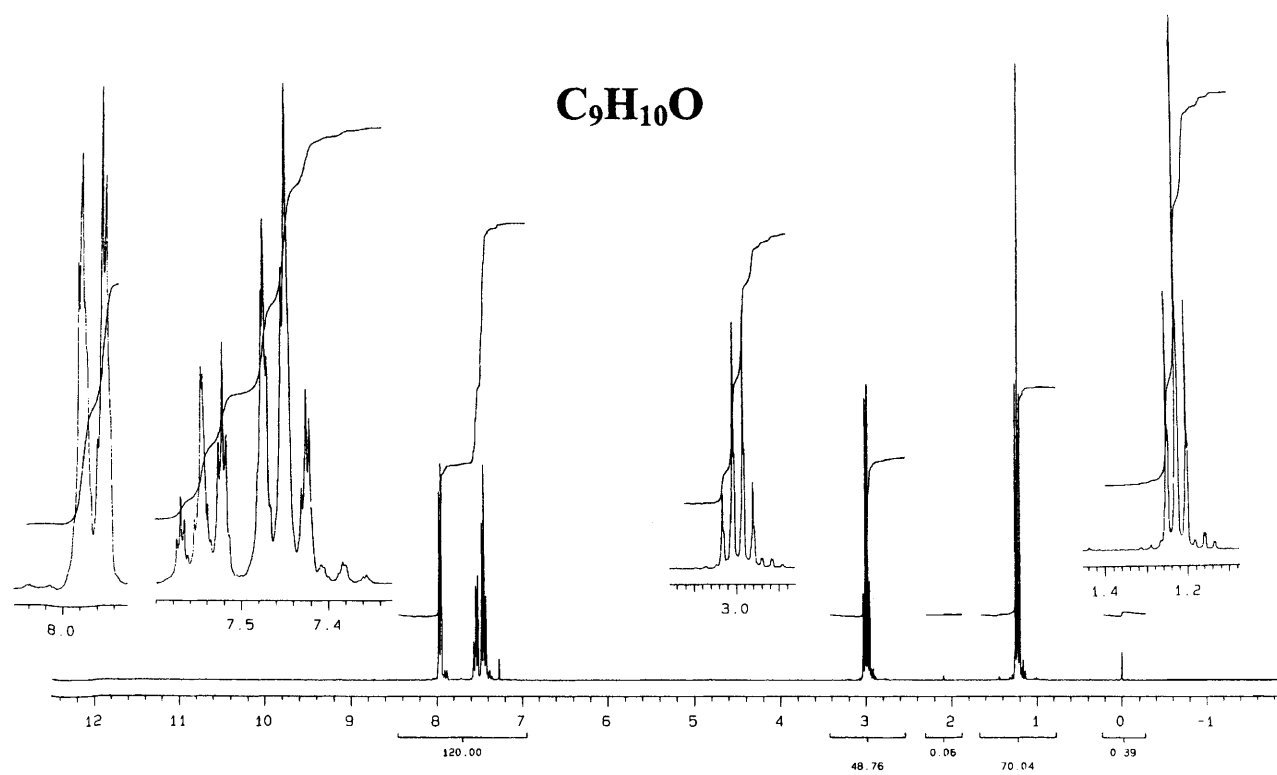




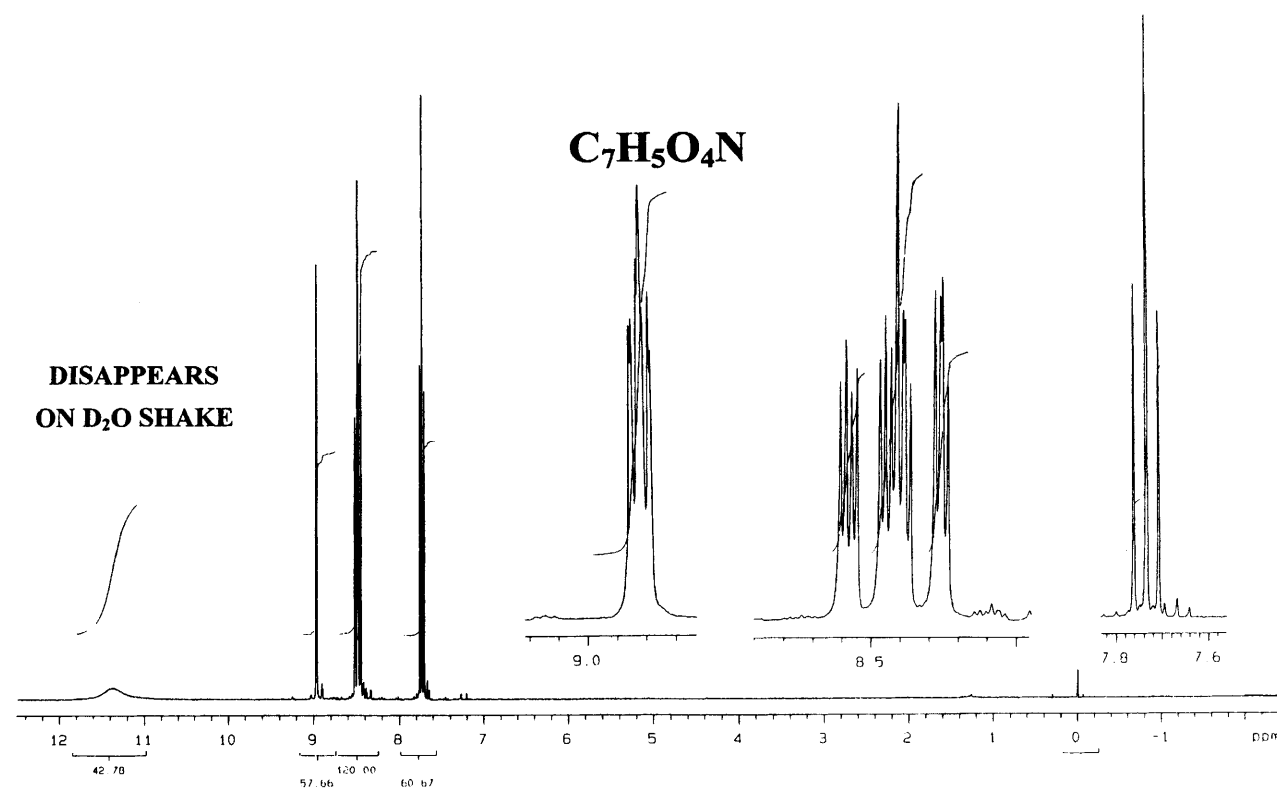
Sample 9.7



Sample 9.8



Sample 9.9

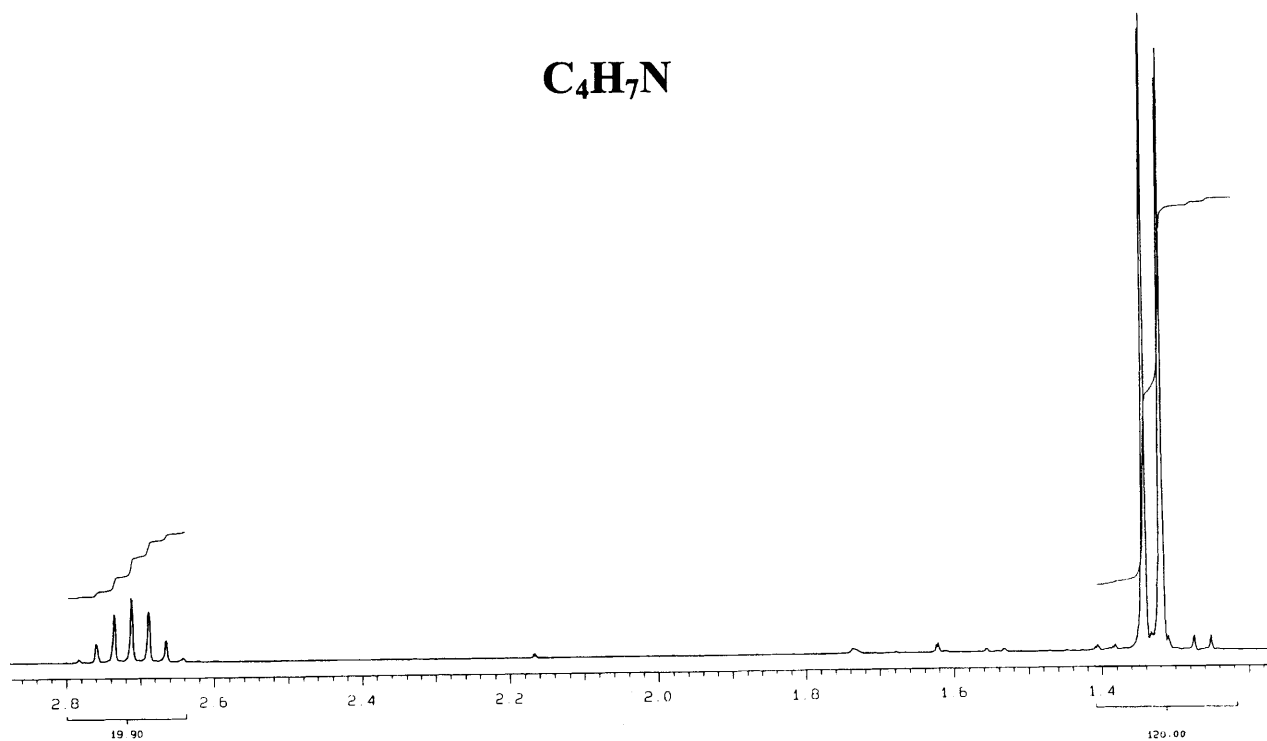
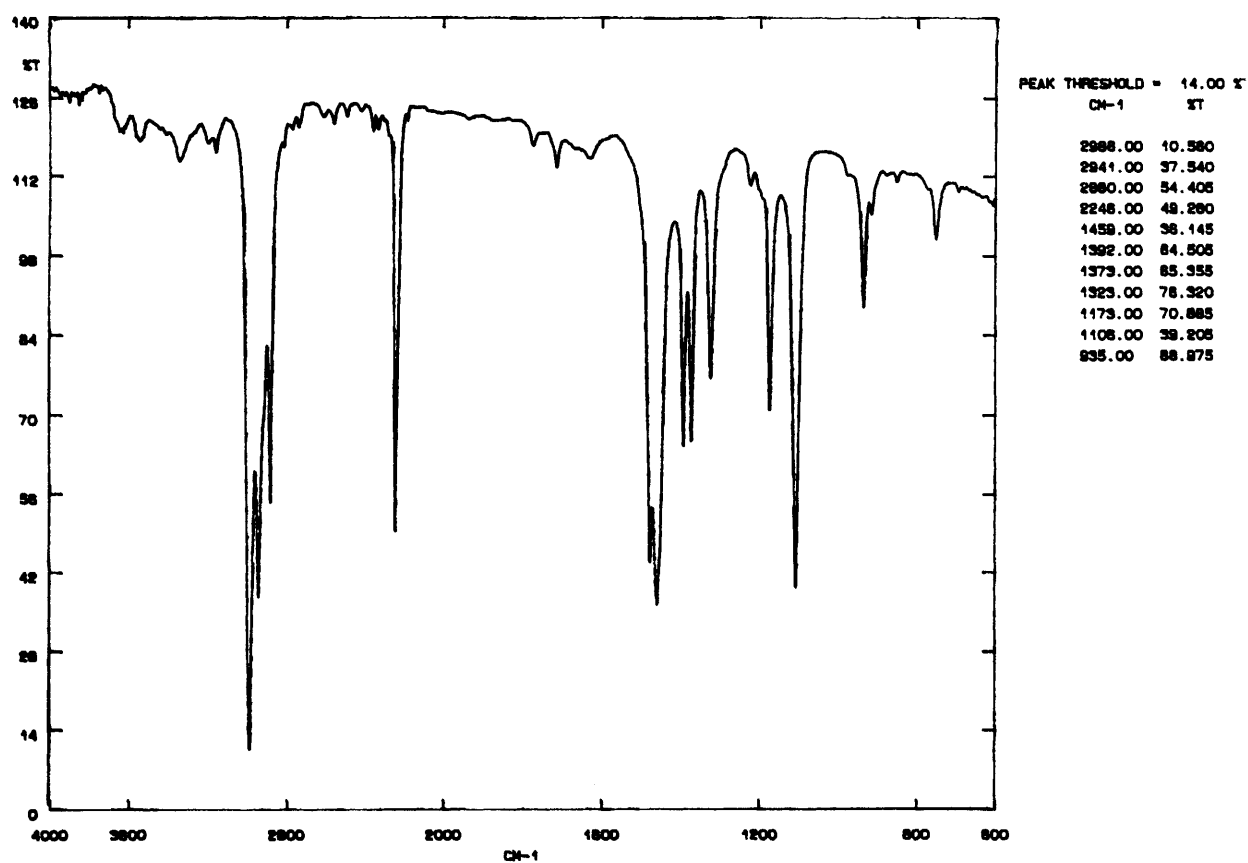


Sample 9.10

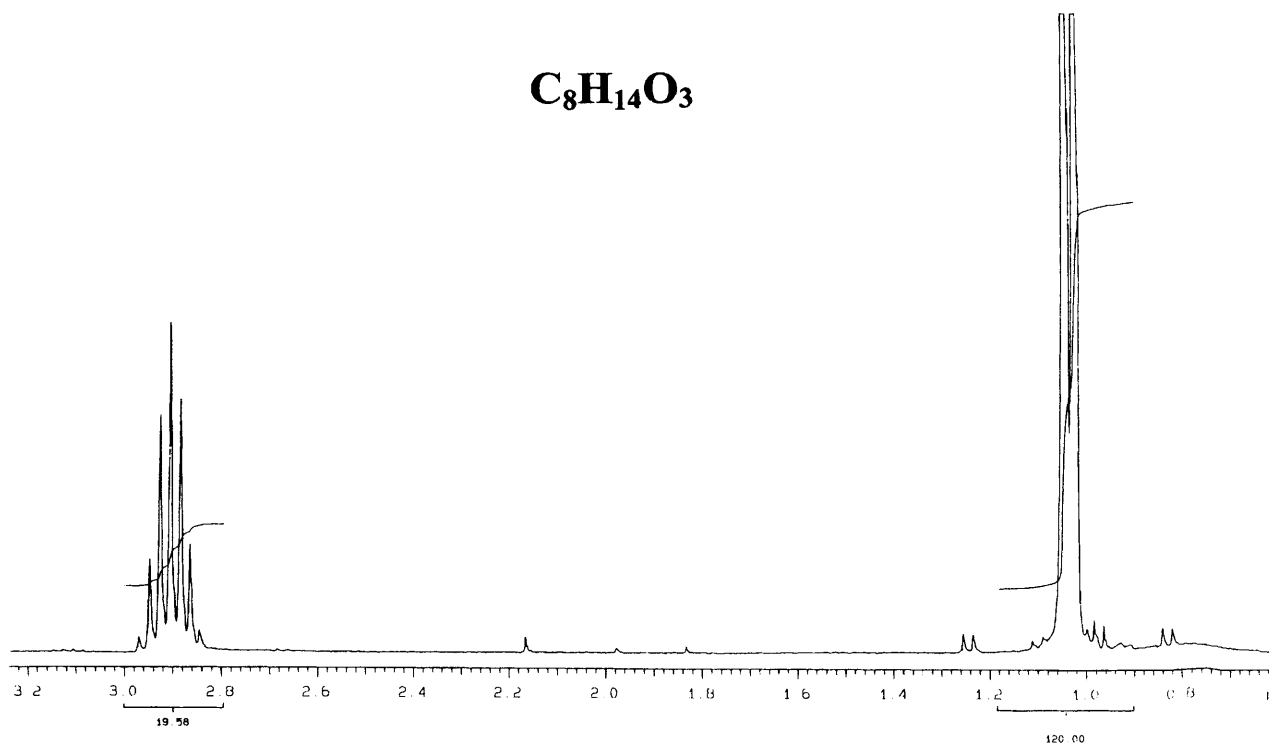
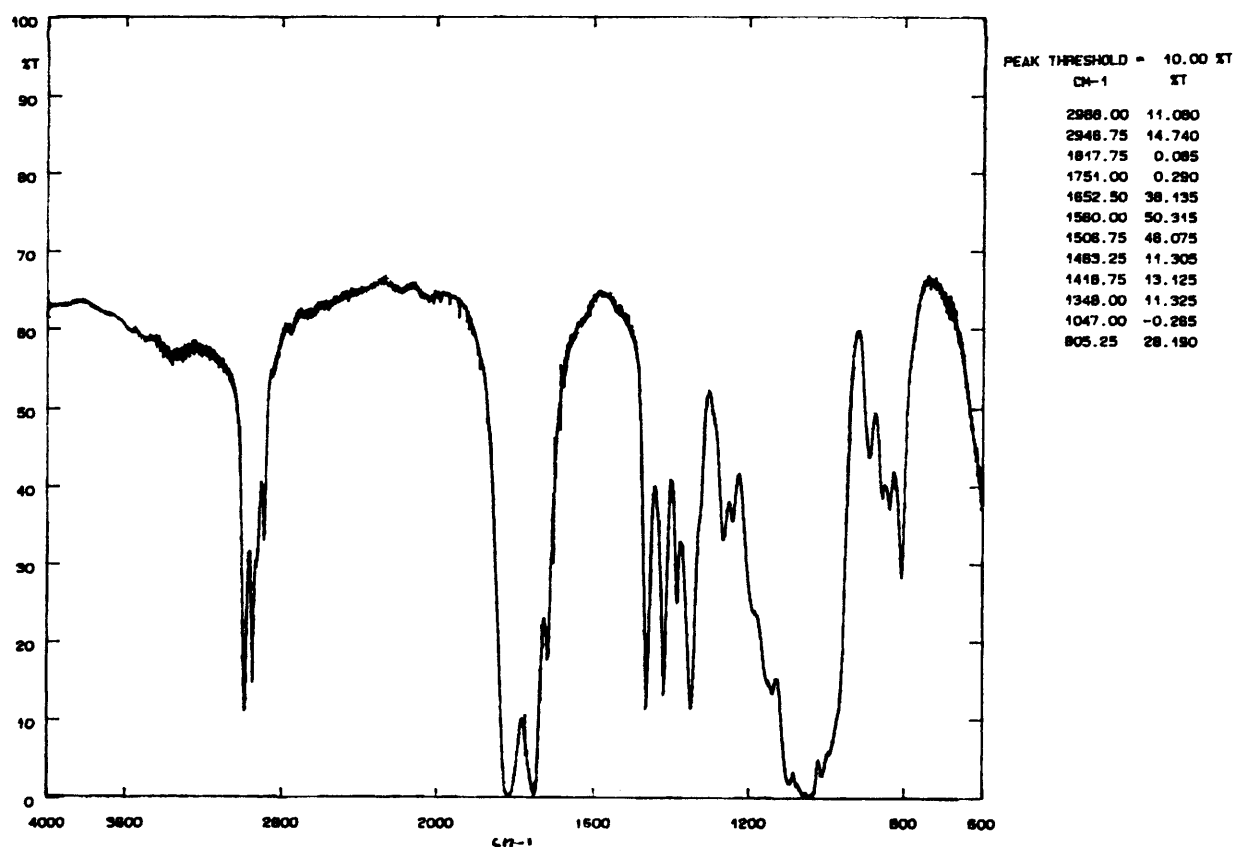
## Problems in Interpreting Infrared and $^1\text{H}$ Nuclear Magnetic Resonance Spectra

$^1\text{H}$  NMR spectroscopy tells us very little about the functional groups present in a molecule. We can detect hydrogen atoms on carbonyl groups, on aromatic rings, on double bonds, on triple bonds and on atoms such as oxygen, nitrogen and sulfur. Even this is more than we were able to manage with  $^{13}\text{C}$  NMR spectroscopy. Consequently,  $^1\text{H}$  NMR and infrared spectroscopy provide a valuable partnership, one identifying the functional groups and the other the structure. Even so, we need to have the molecular formula provided, as neither technique will give conclusive evidence for the presence of halogens, and it is essential to know how many hydrogen atoms a molecule has before we attempt to assign the  $^1\text{H}$  NMR spectrum.

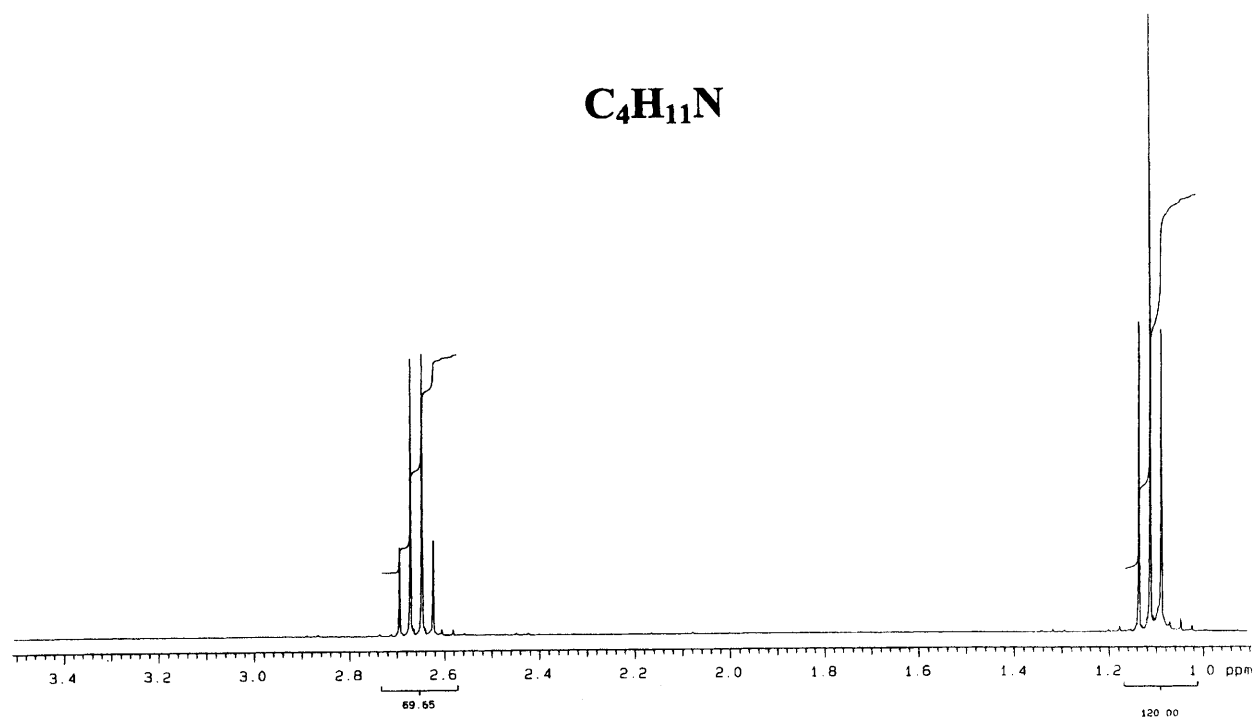
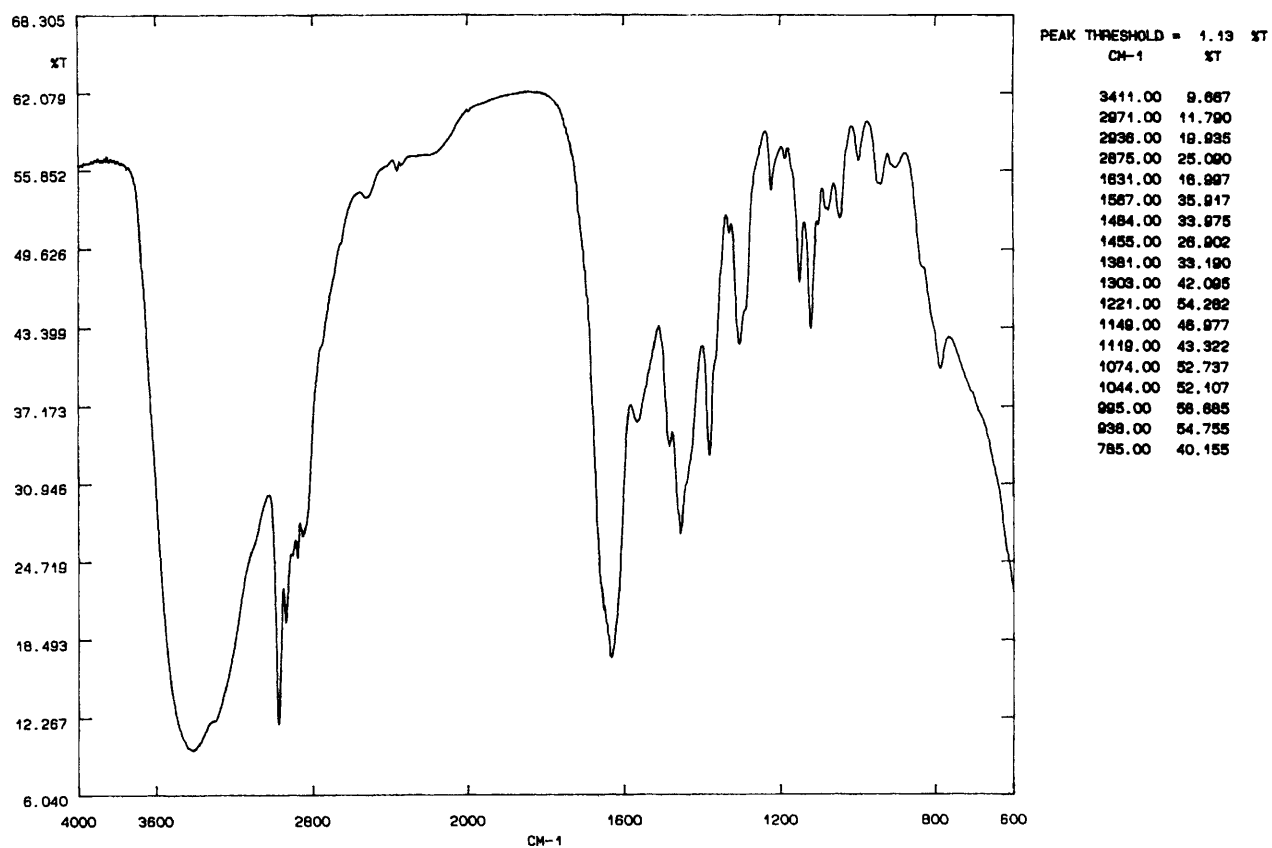
In this exercise, all the necessary data are provided for 10 substances. You should be able to identify them from this information.



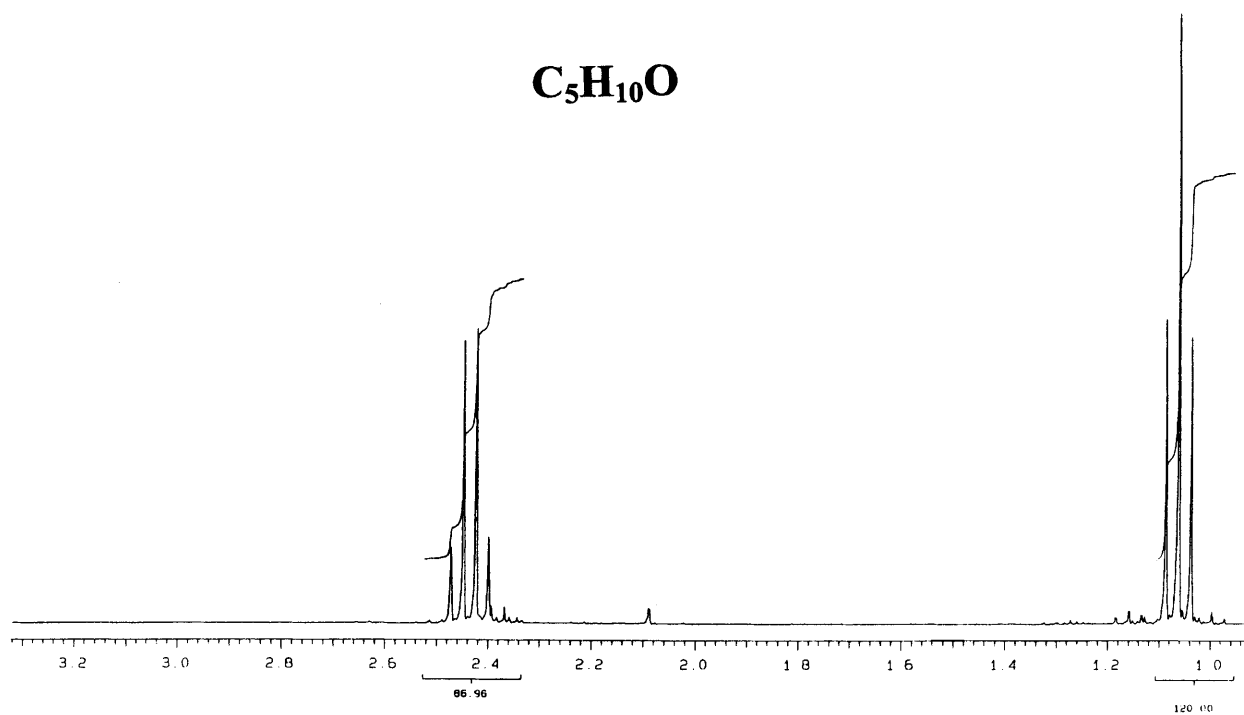
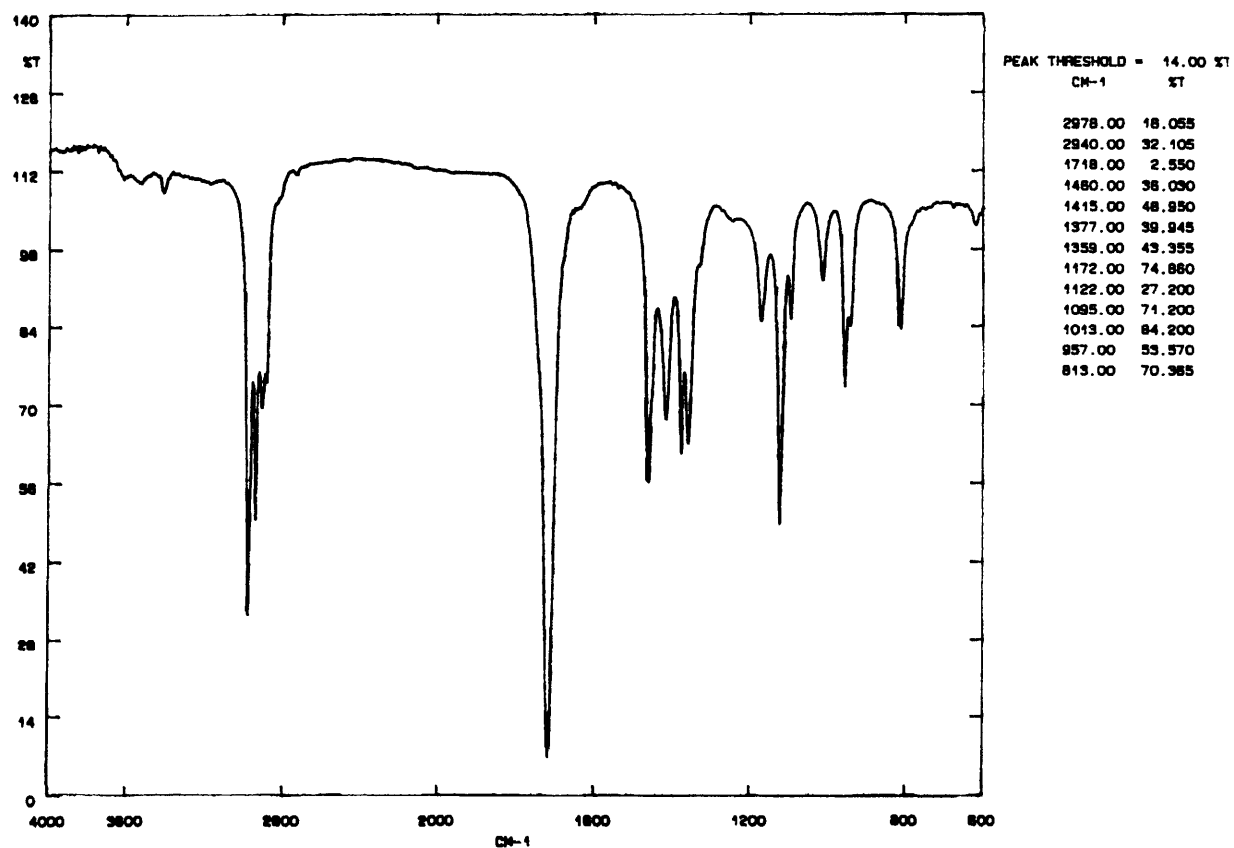
Sample 10.1



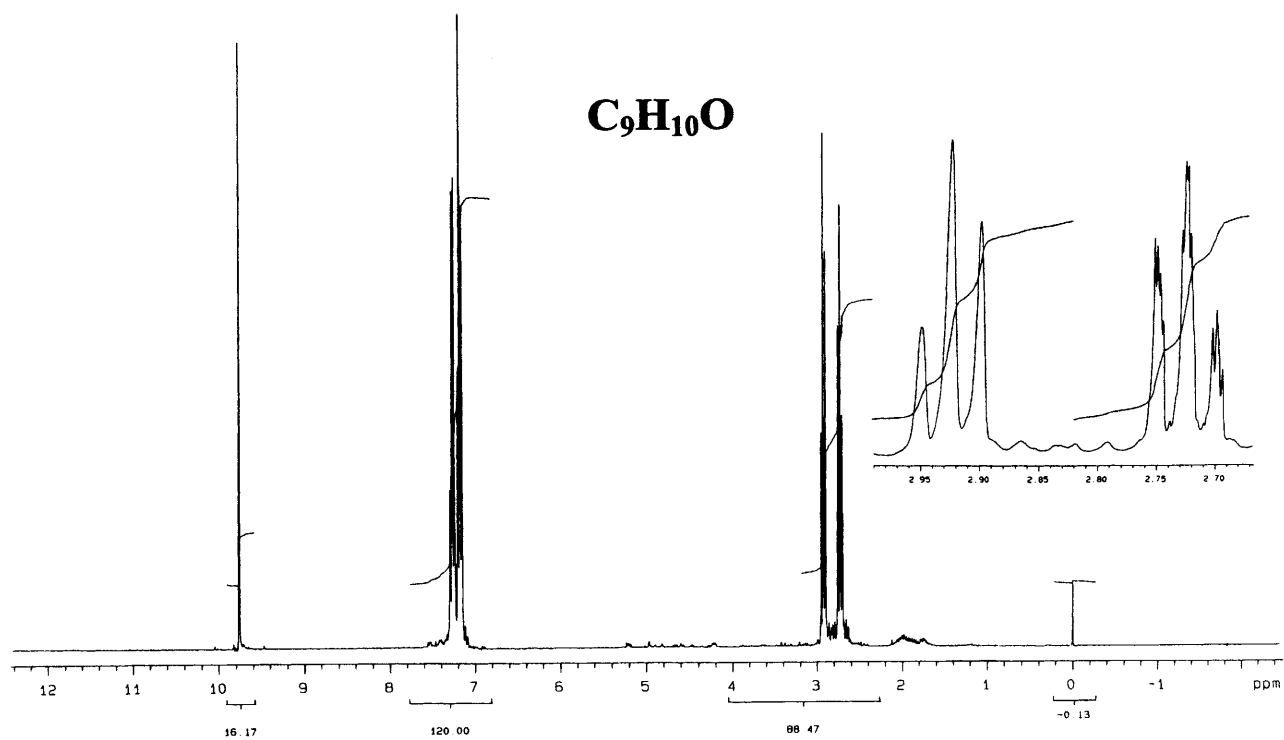
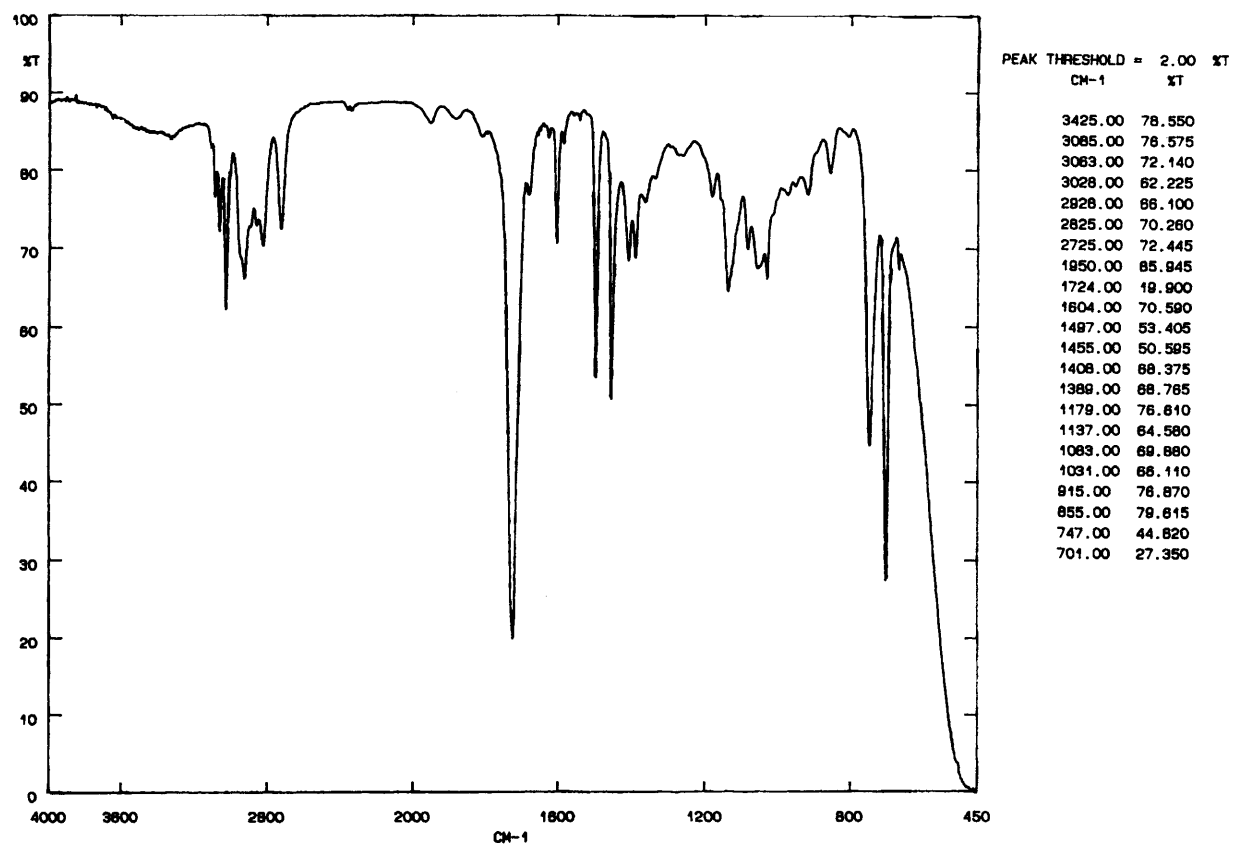
Sample 10.2



Sample 10.3

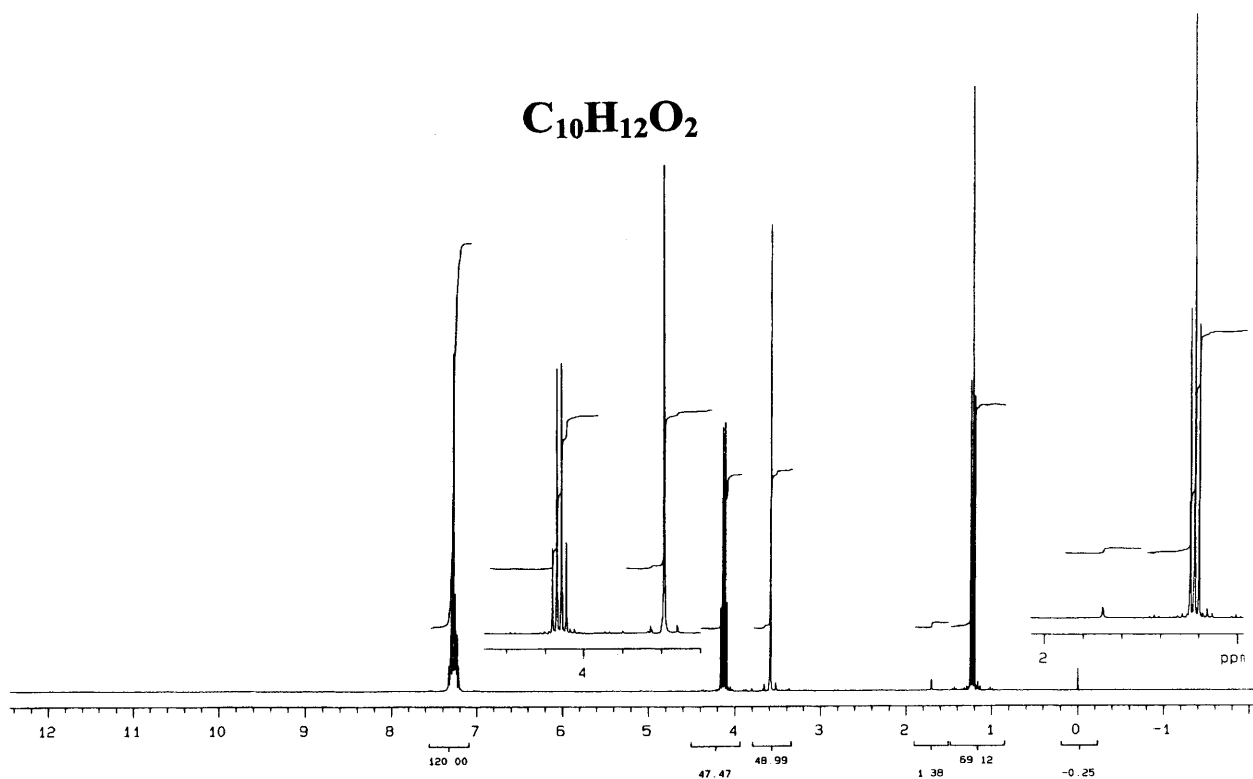
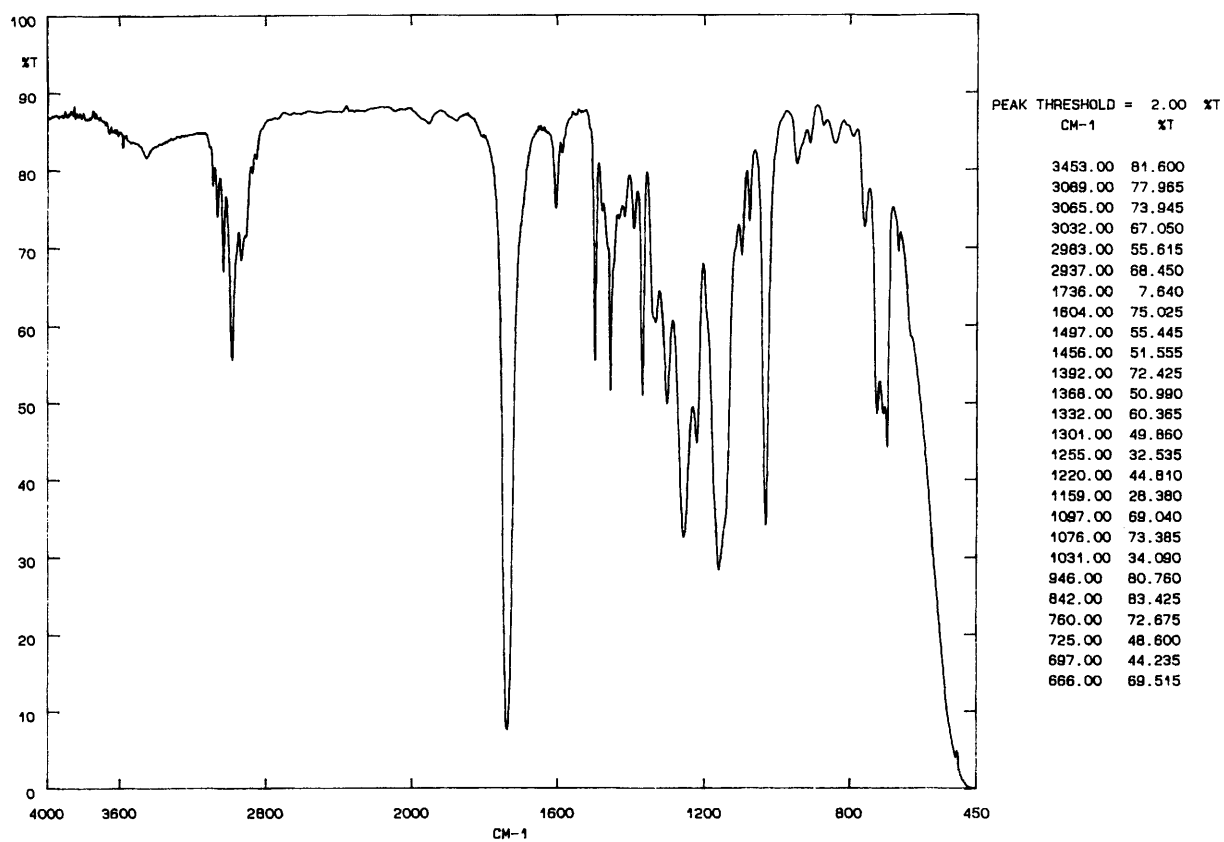


Sample 10.4

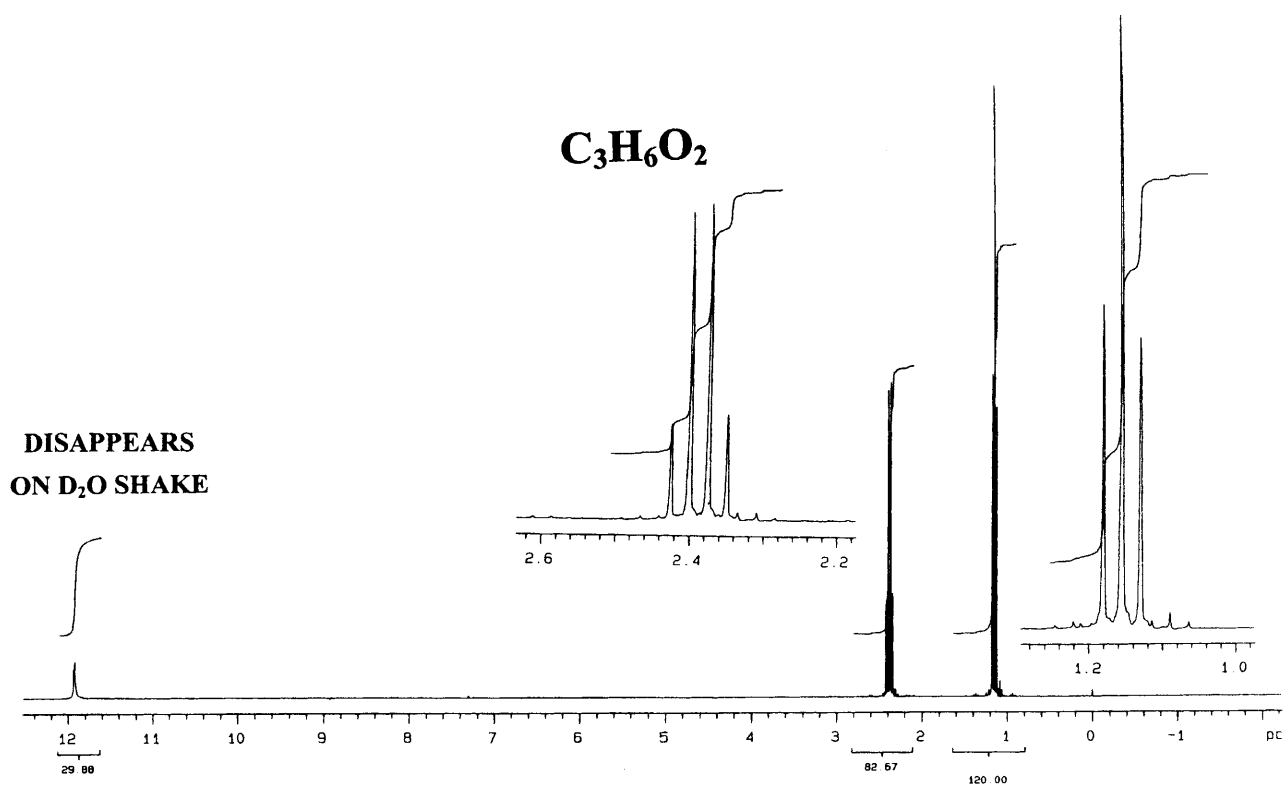
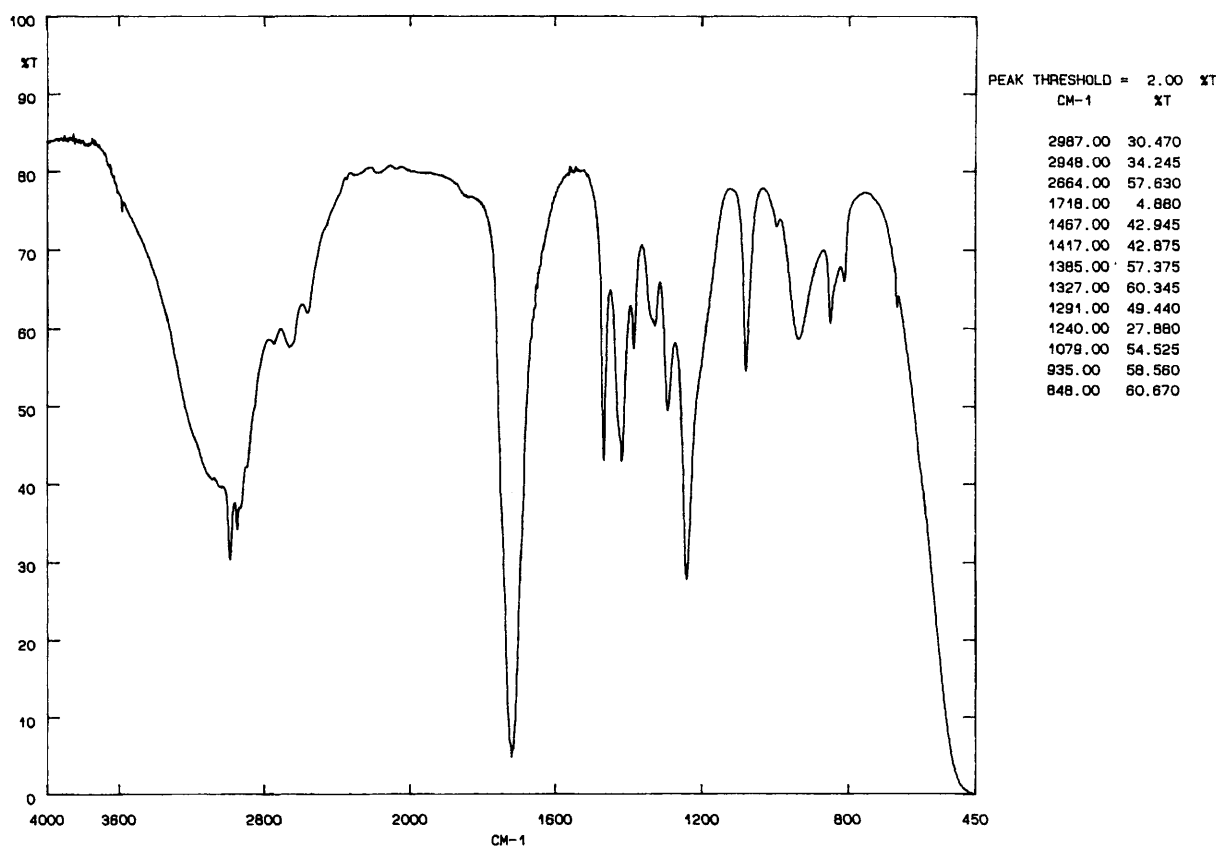


Sample 10.5

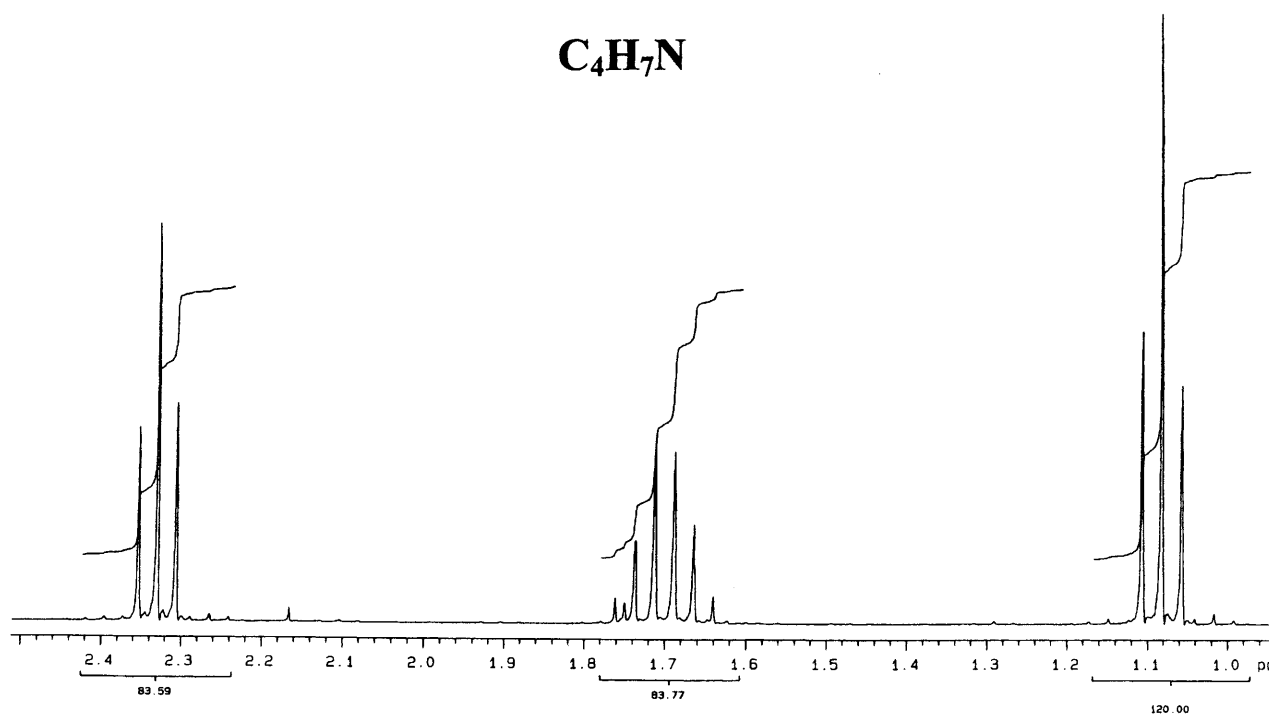
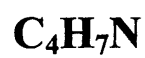
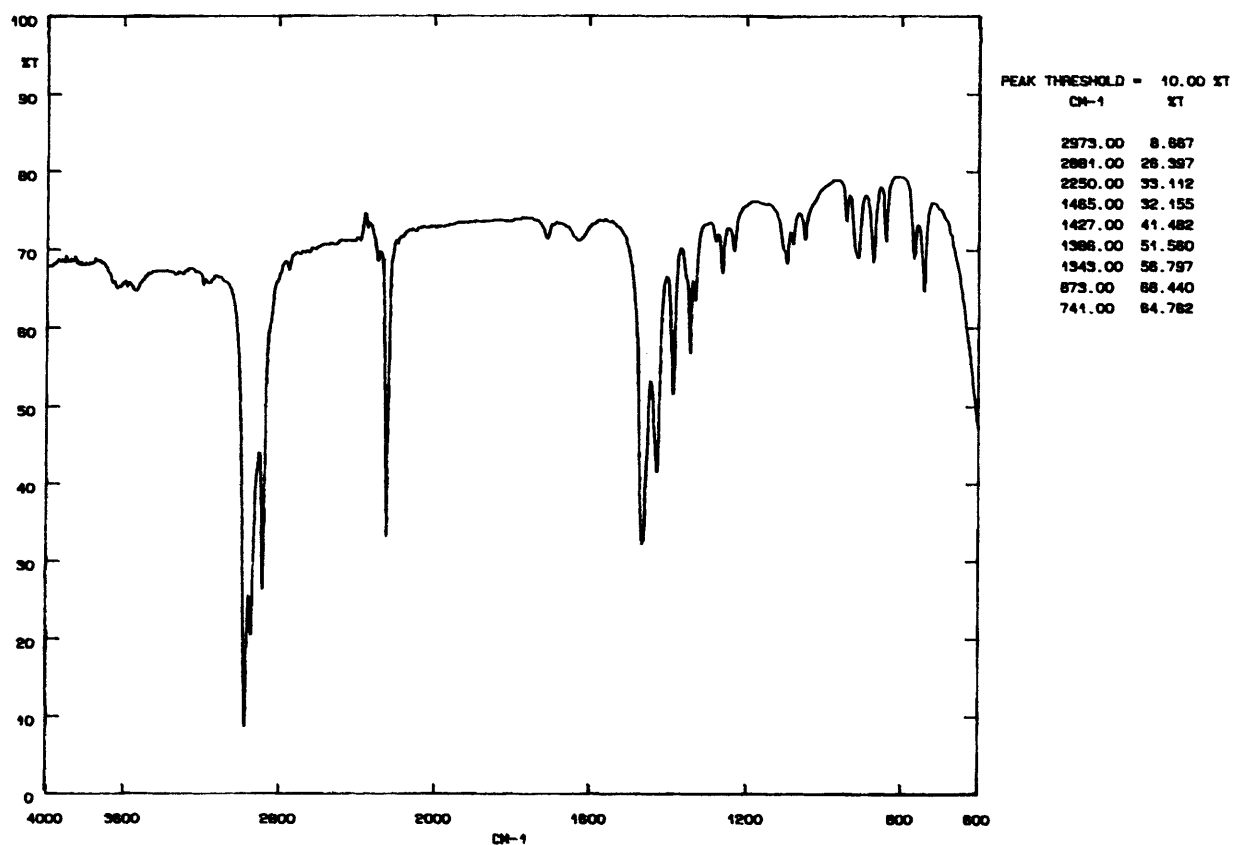




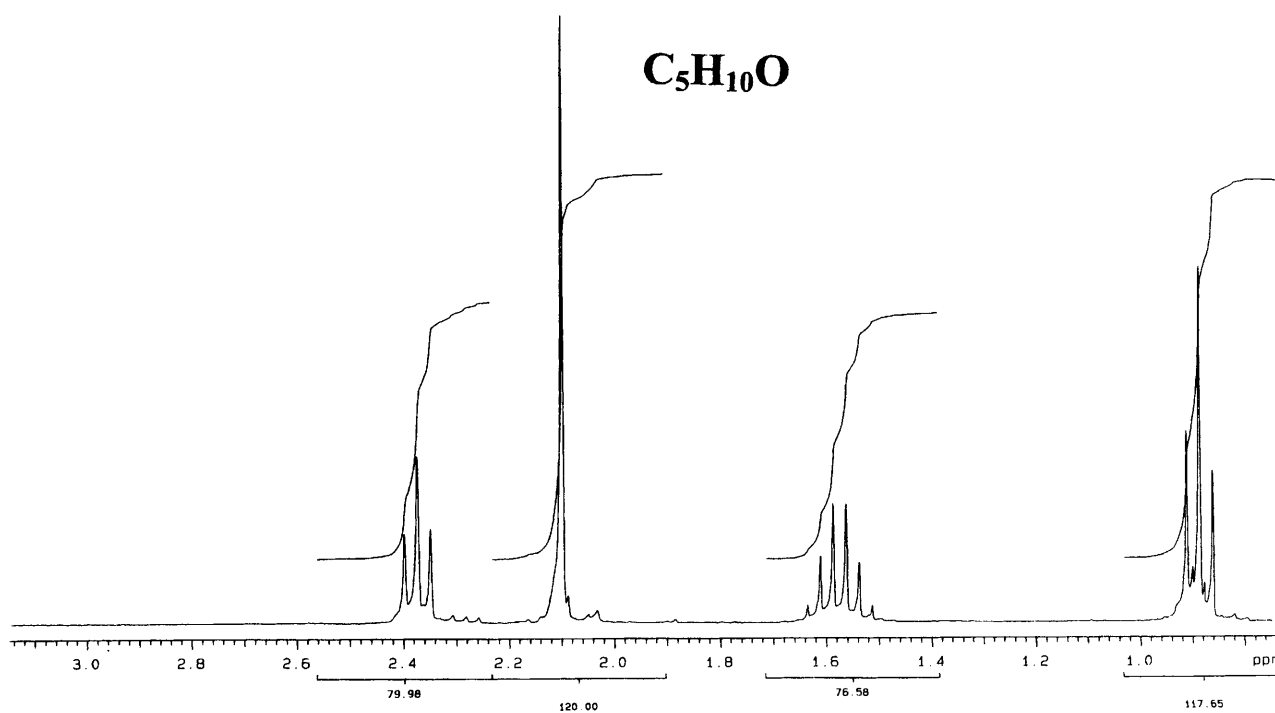
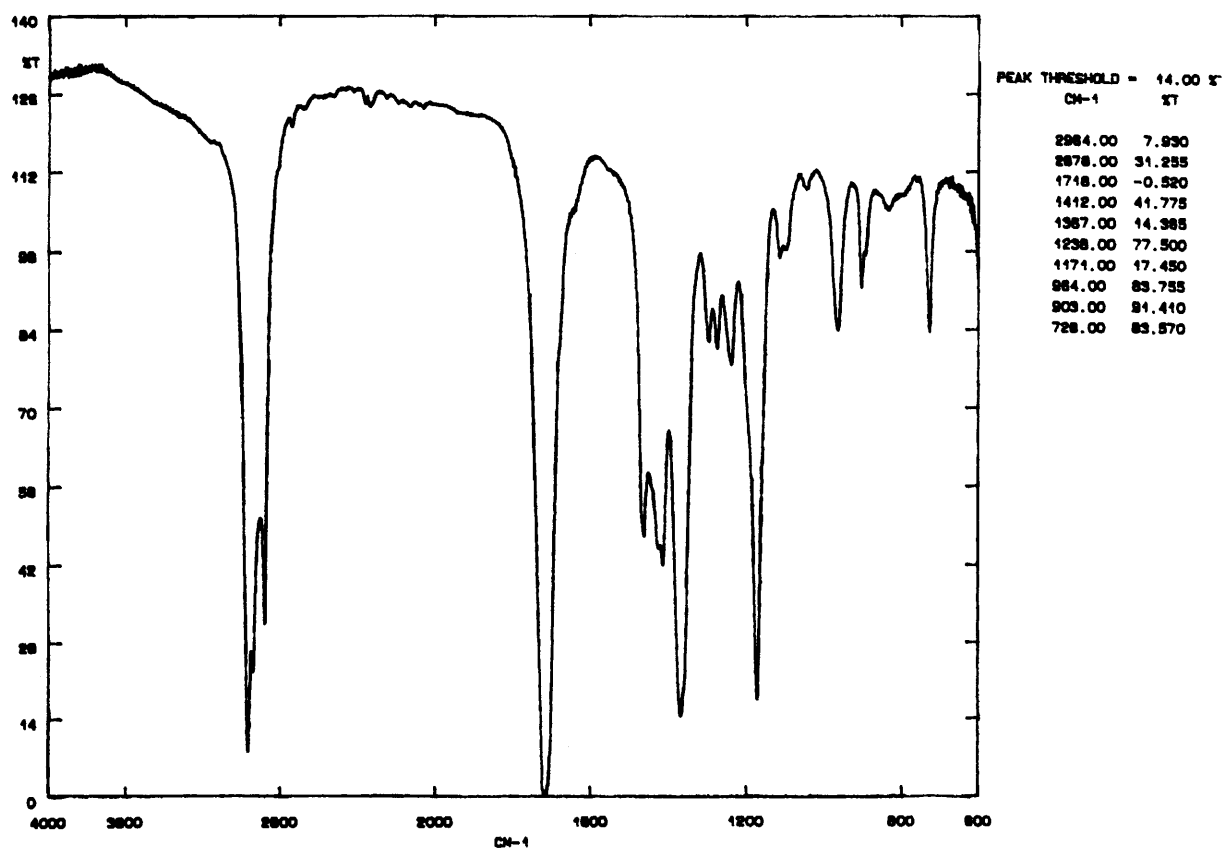
Sample 10.6



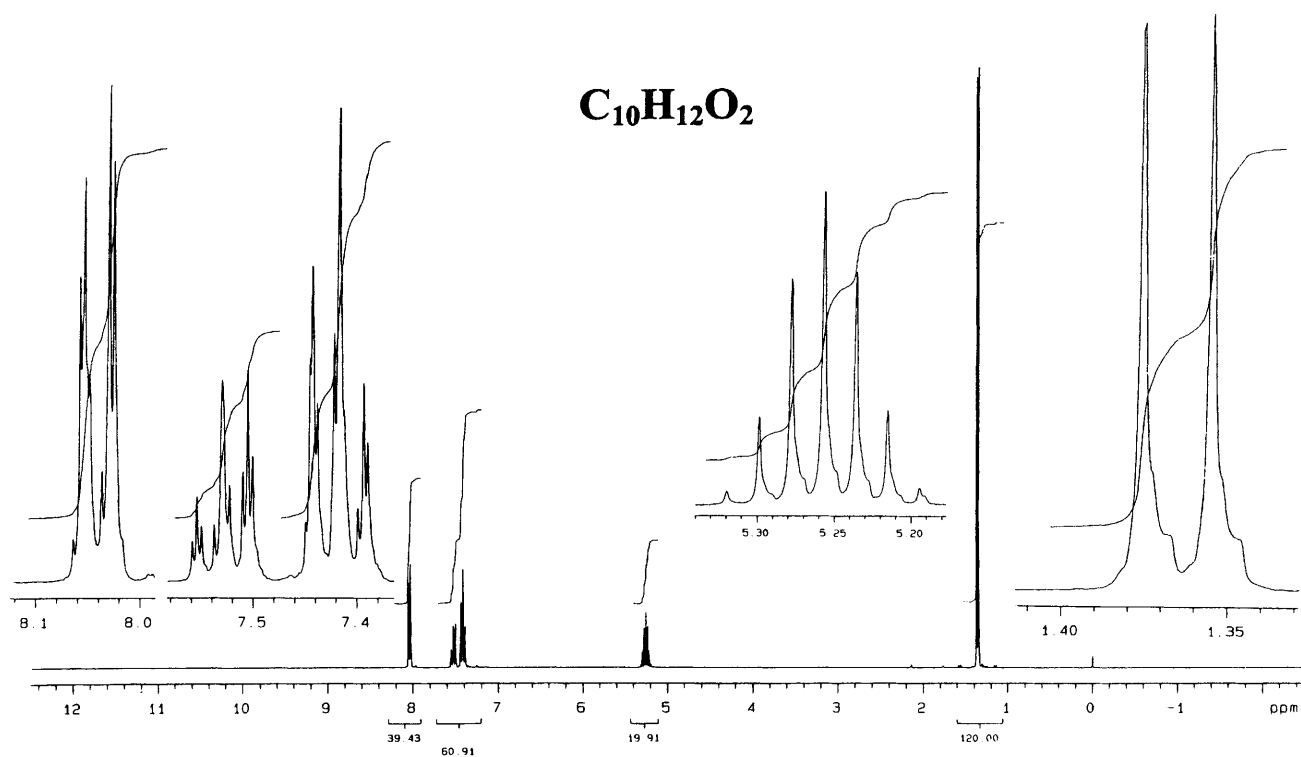
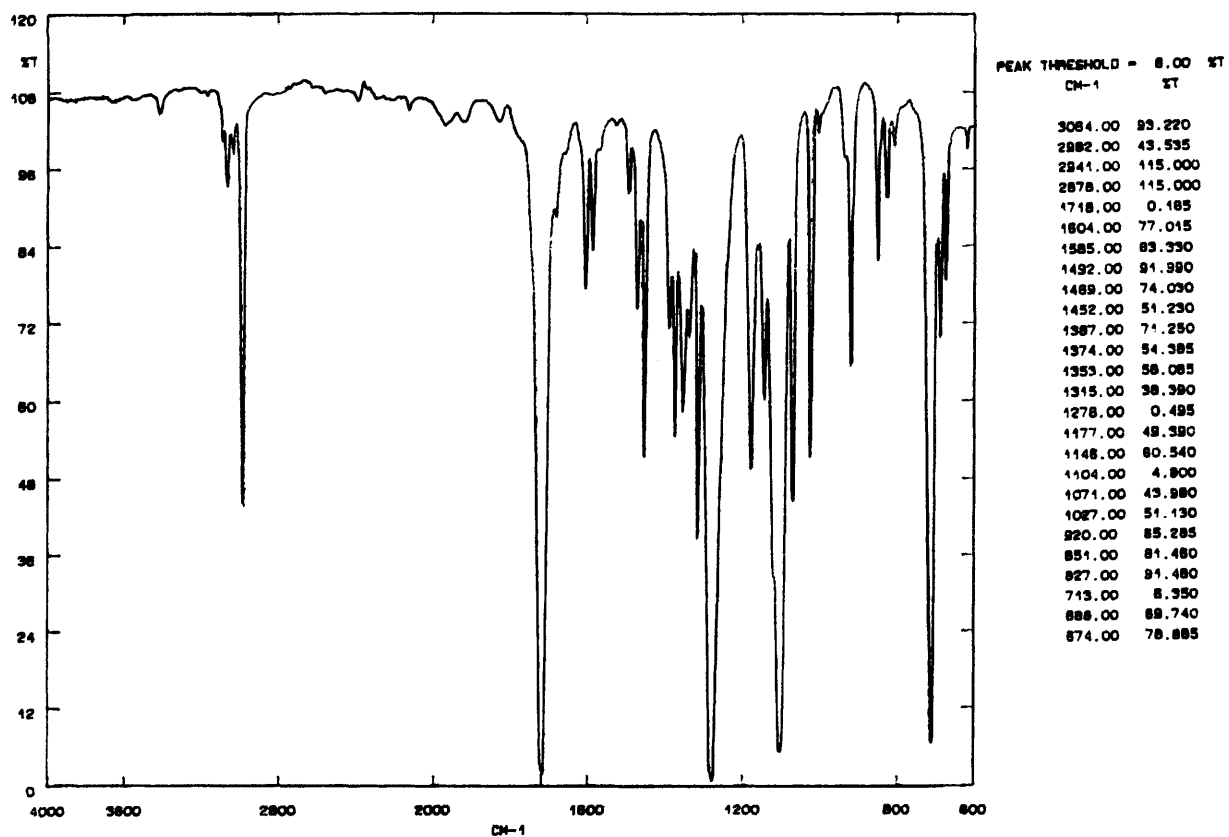
Sample 10.7



Sample 10.8



Sample 10.9



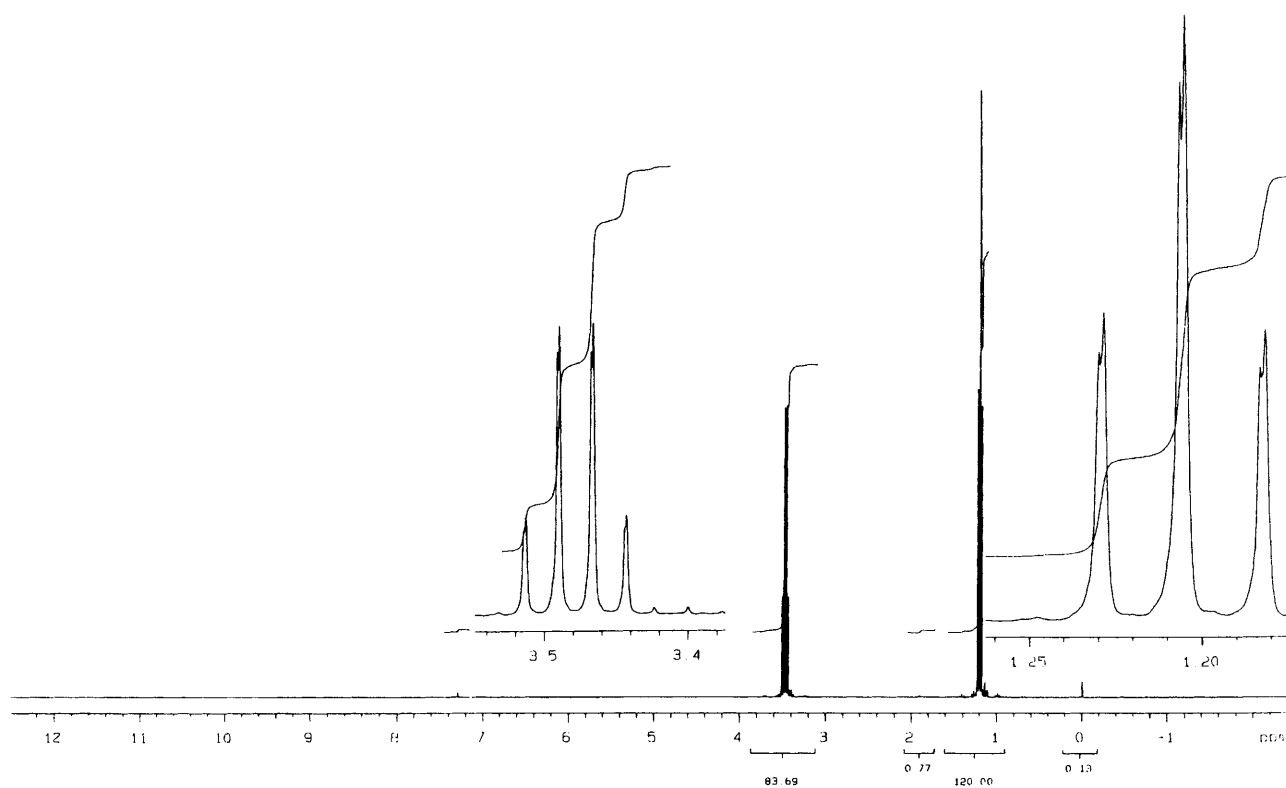
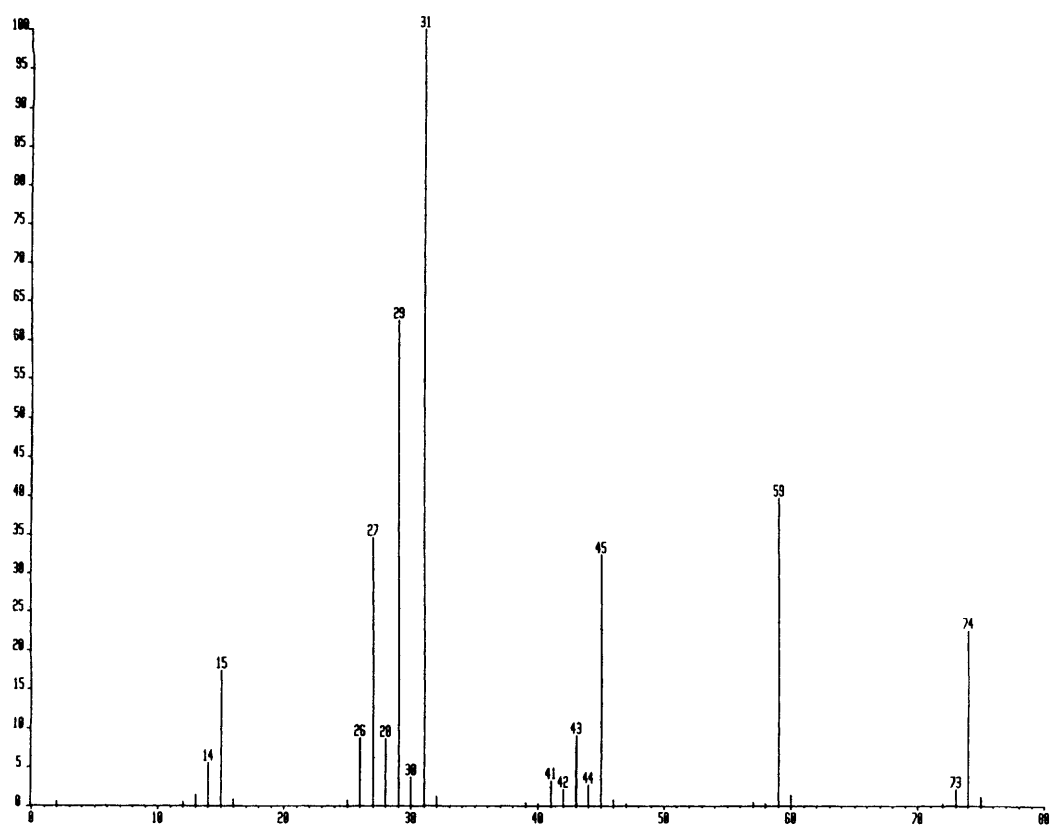
Sample 10.10



## Problems in Interpreting Mass Spectra and $^1\text{H}$ Nuclear Magnetic Resonance Spectra

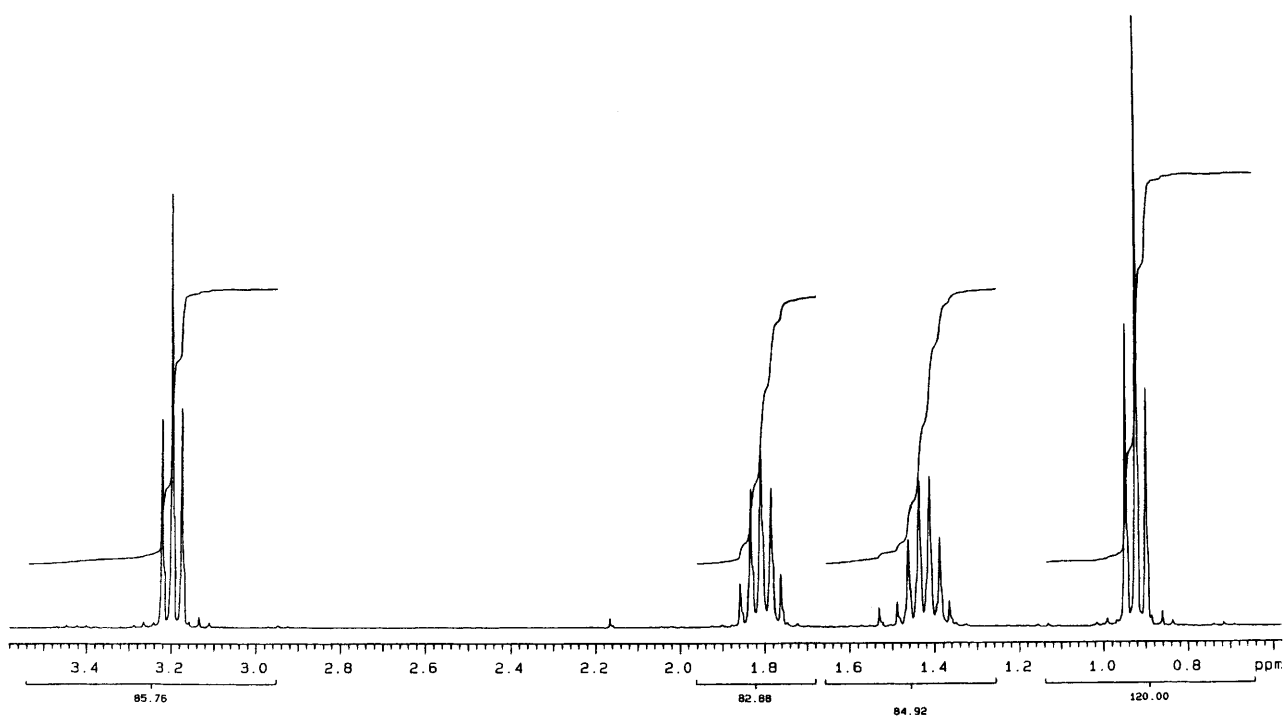
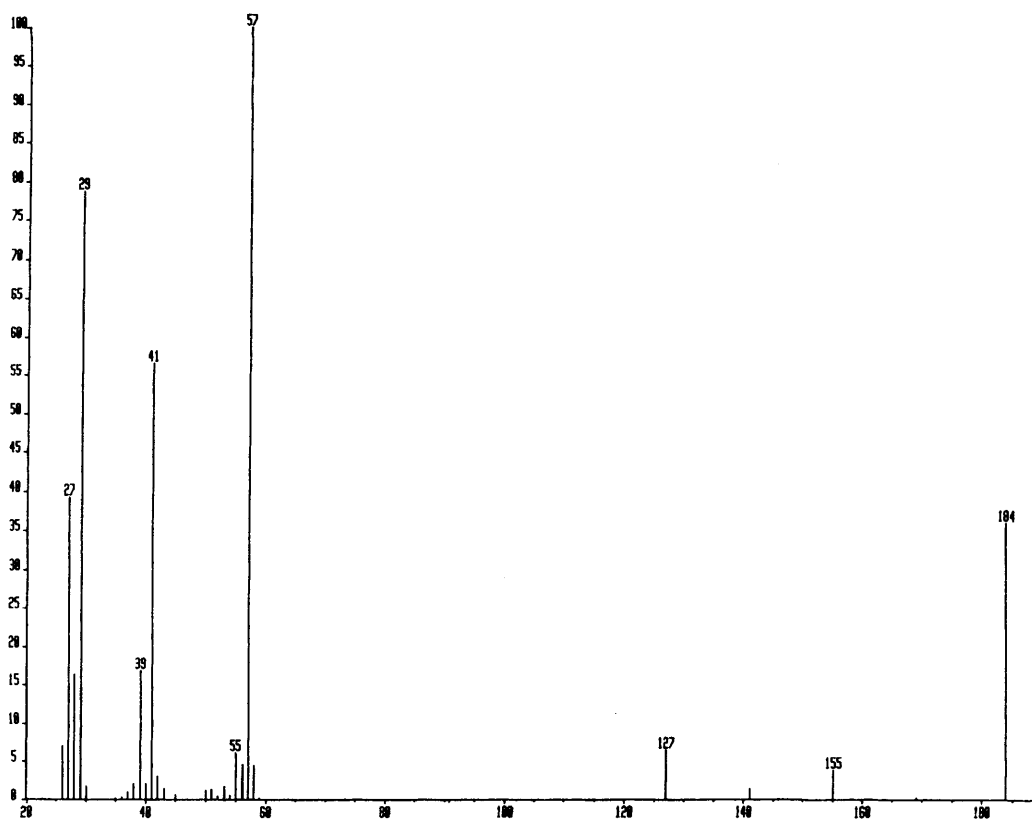
When we combine mass spectrometry with  $^1\text{H}$  NMR spectroscopy we no longer need to supply molecular formulae. It is often a problem to determine the number of hydrogen atoms in a molecule when the integration is uncertain, and it may be best to try to sort out the groups in the molecule and then see how close this comes to the molecular weight. Although  $^1\text{H}$  NMR is an excellent method for determining structures, the mass spectra must not be ignored—observation, for example, of a McLafferty rearrangement gives a great deal of structural information about a molecule. The mass spectrum can also reveal information about the presence of halogen atoms, and the molecular weight, when compared to the  $^1\text{H}$  NMR data, can reveal the presence of a plane of symmetry in the molecule.

In this exercise, the mass spectra and  $^1\text{H}$  NMR spectra of 10 samples are provided. You should be able to identify all the samples from the data.

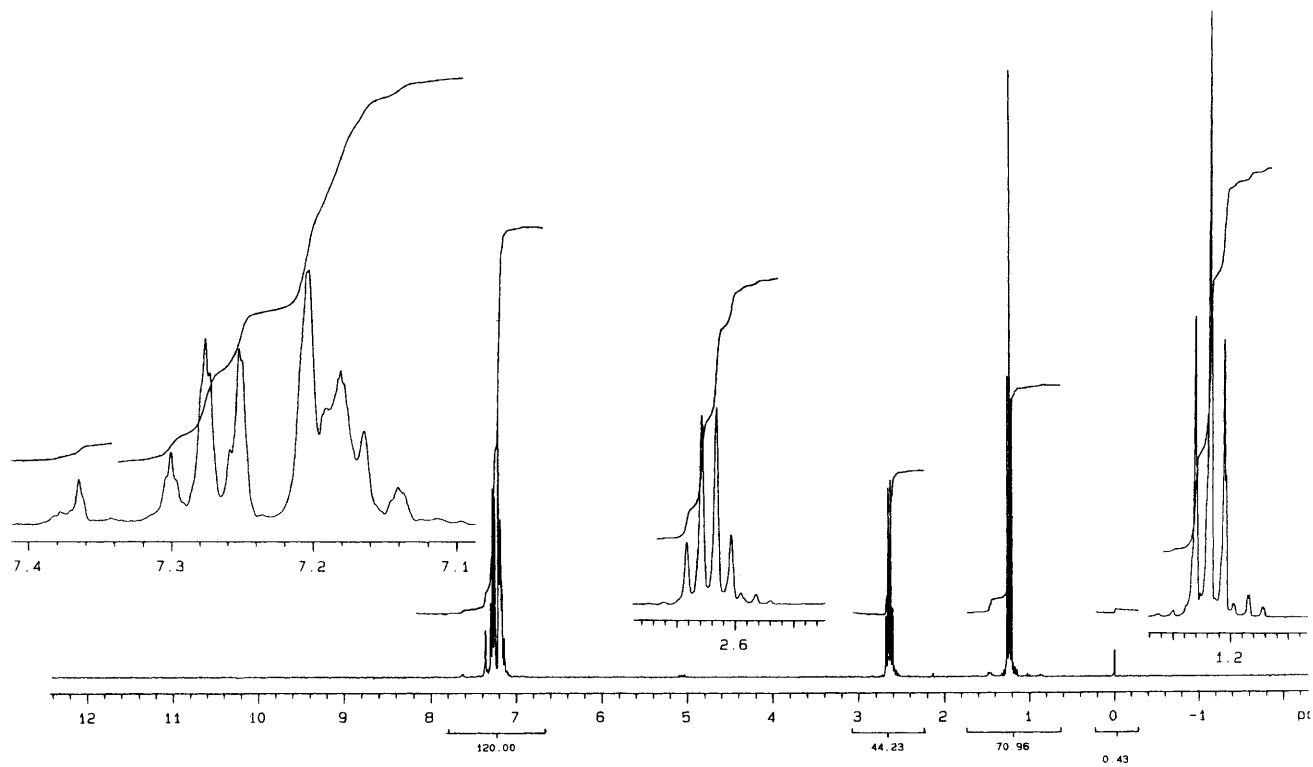
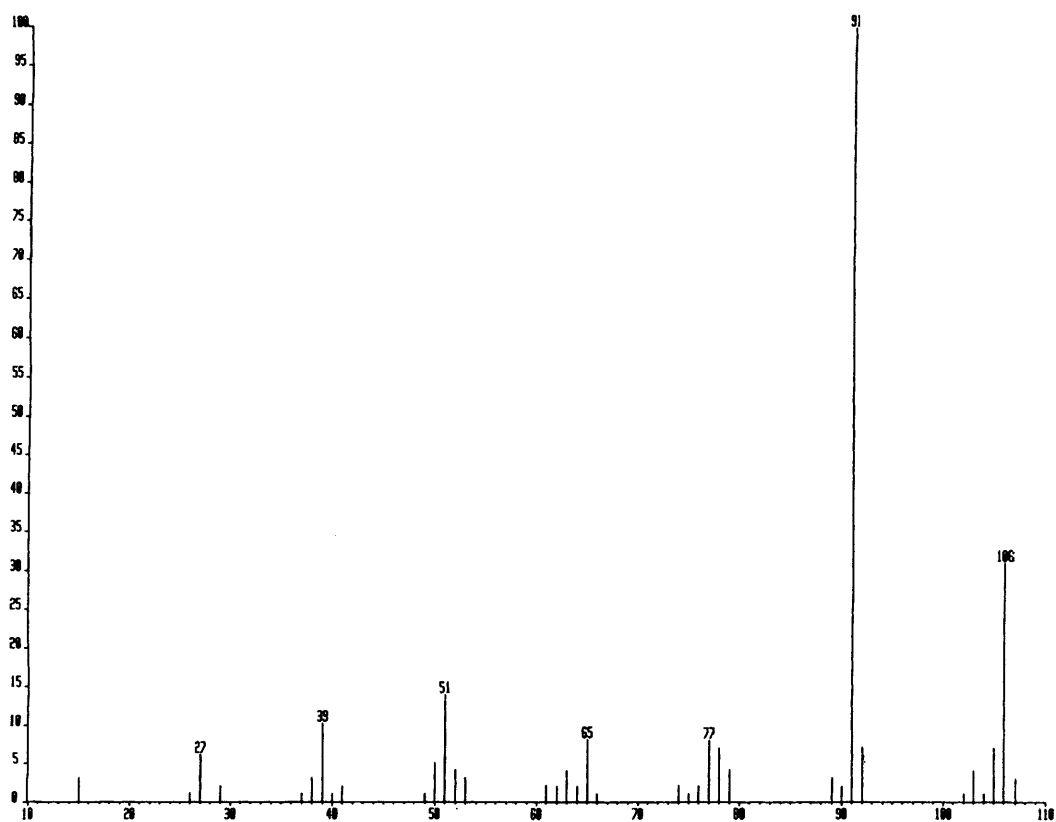


Sample 11.1

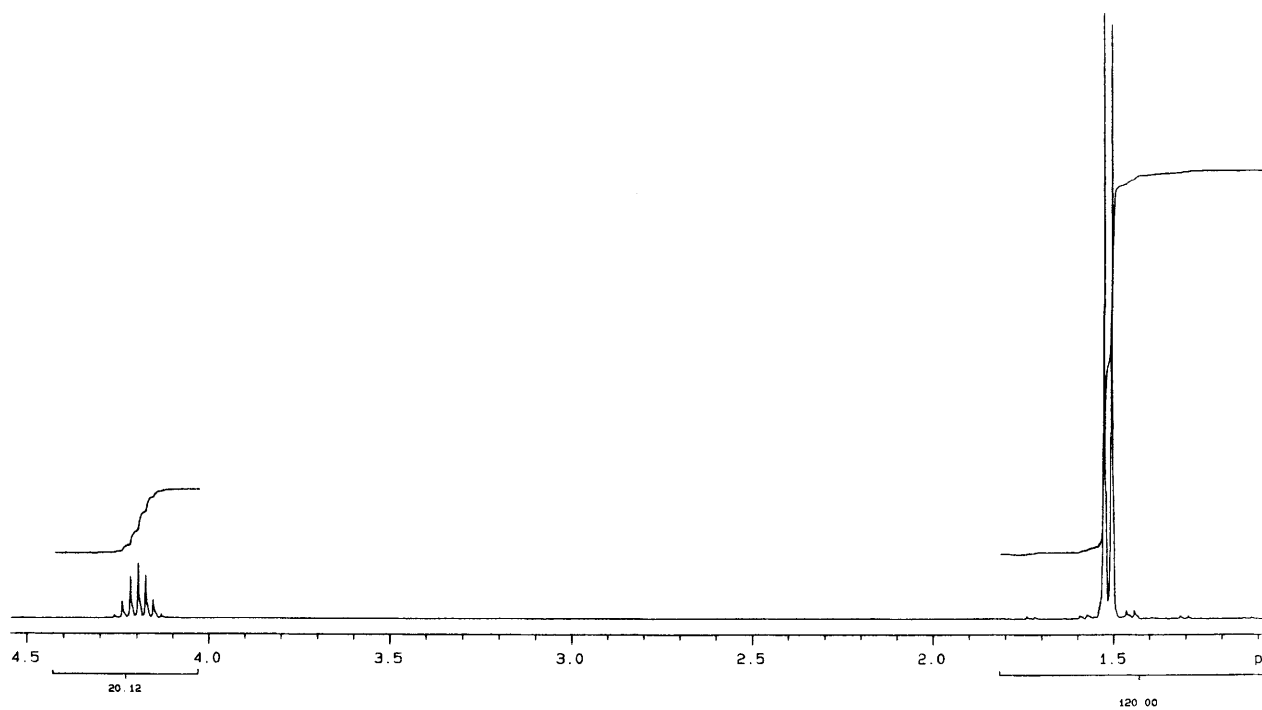
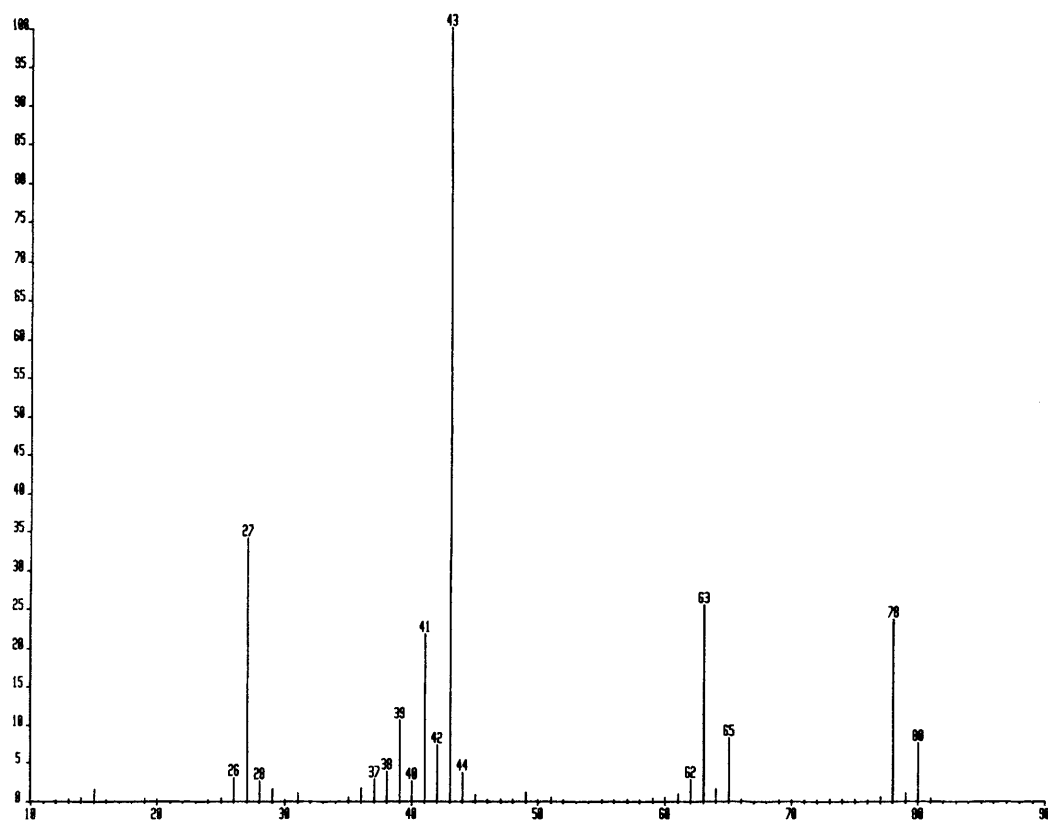




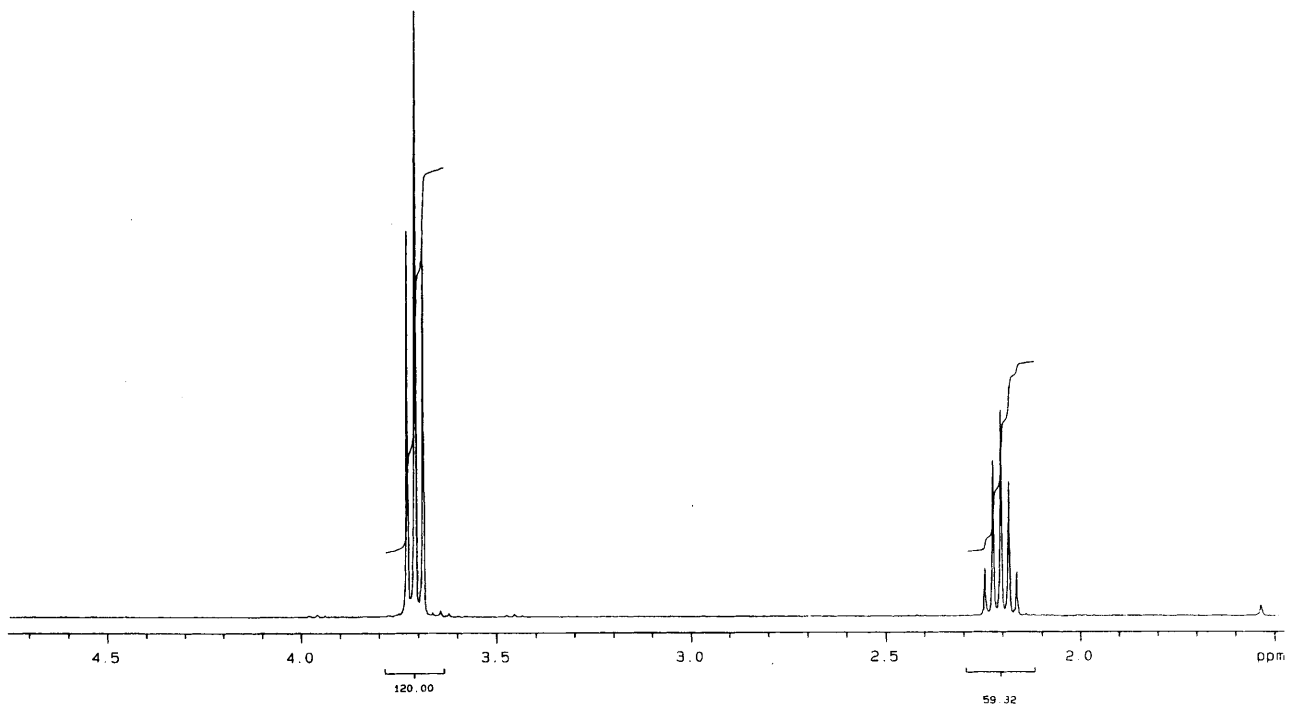
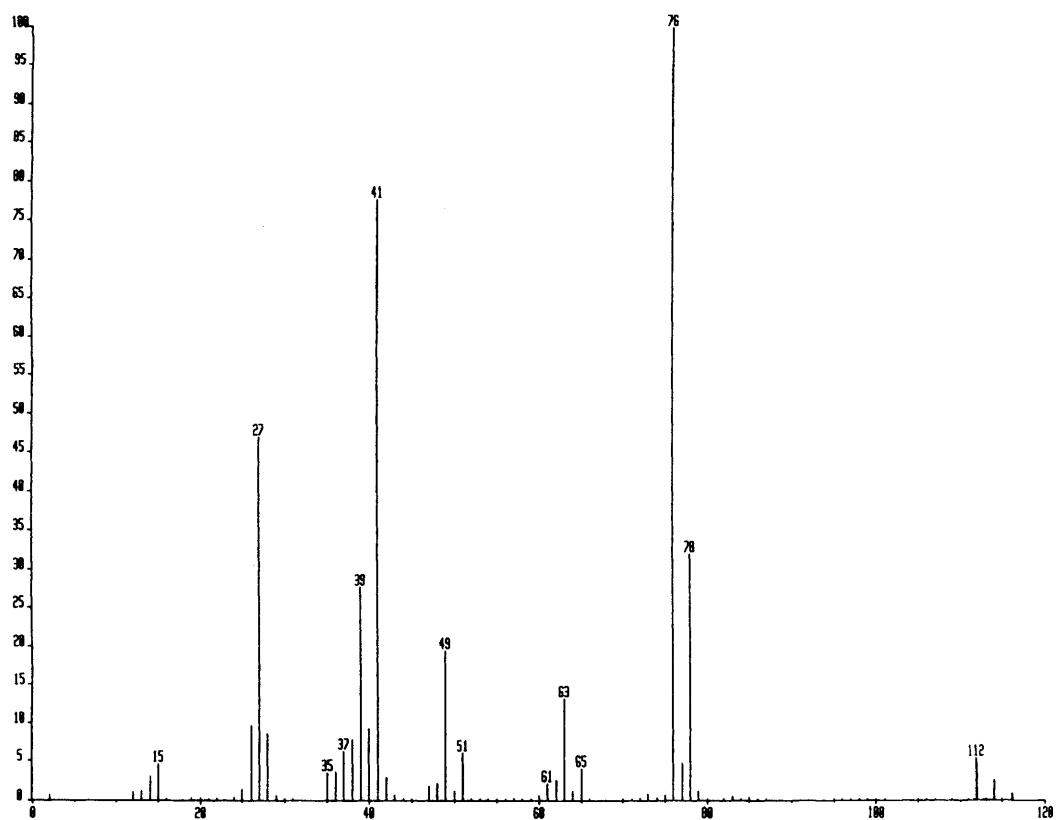
Sample 11.2



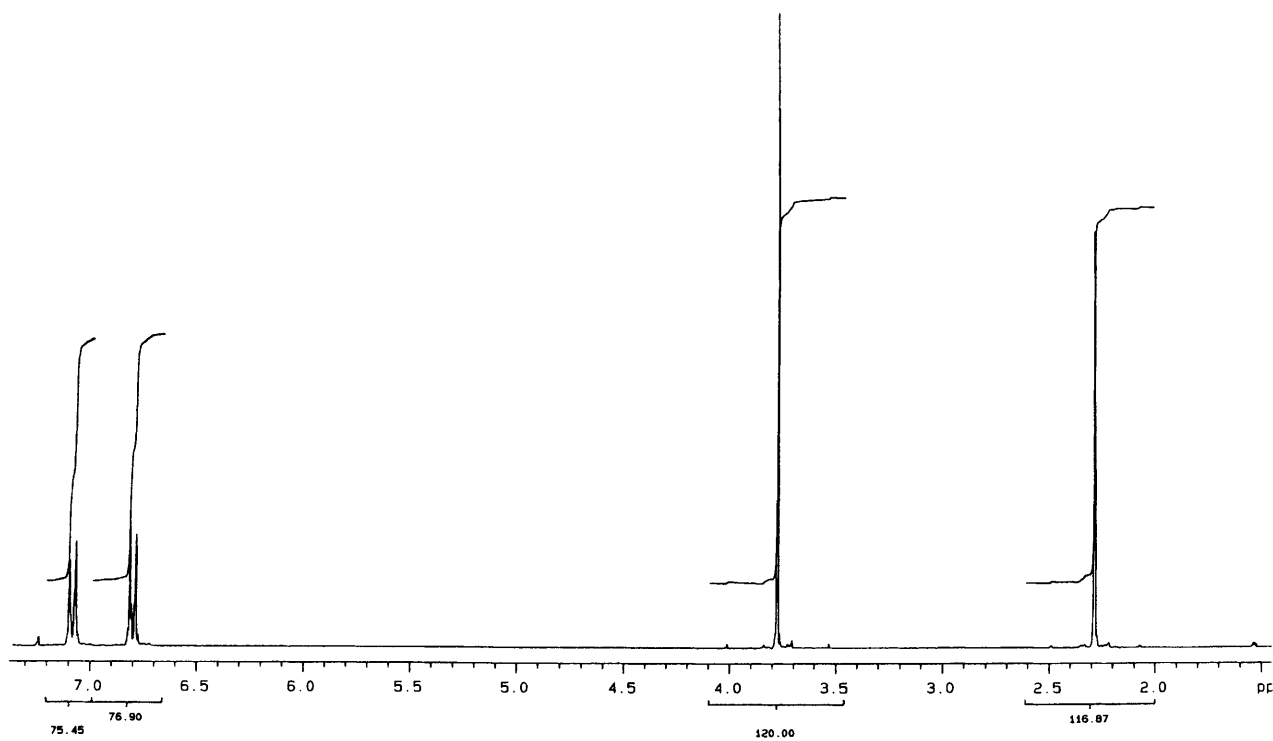
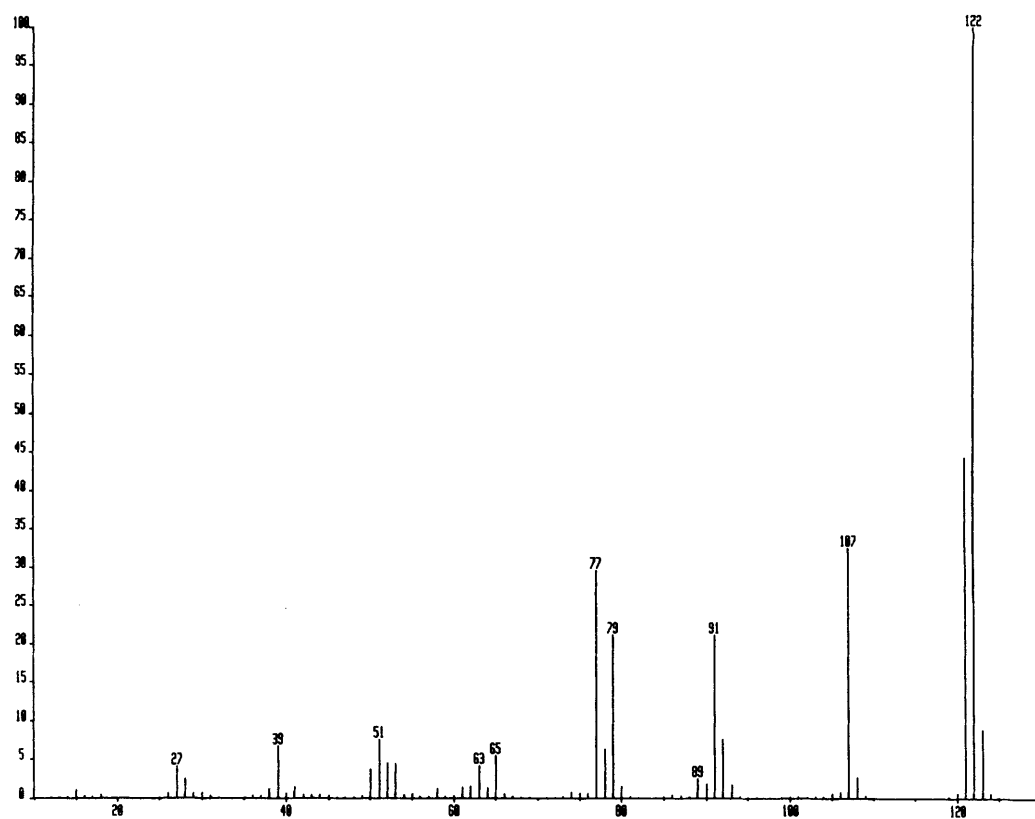
Sample 11.3



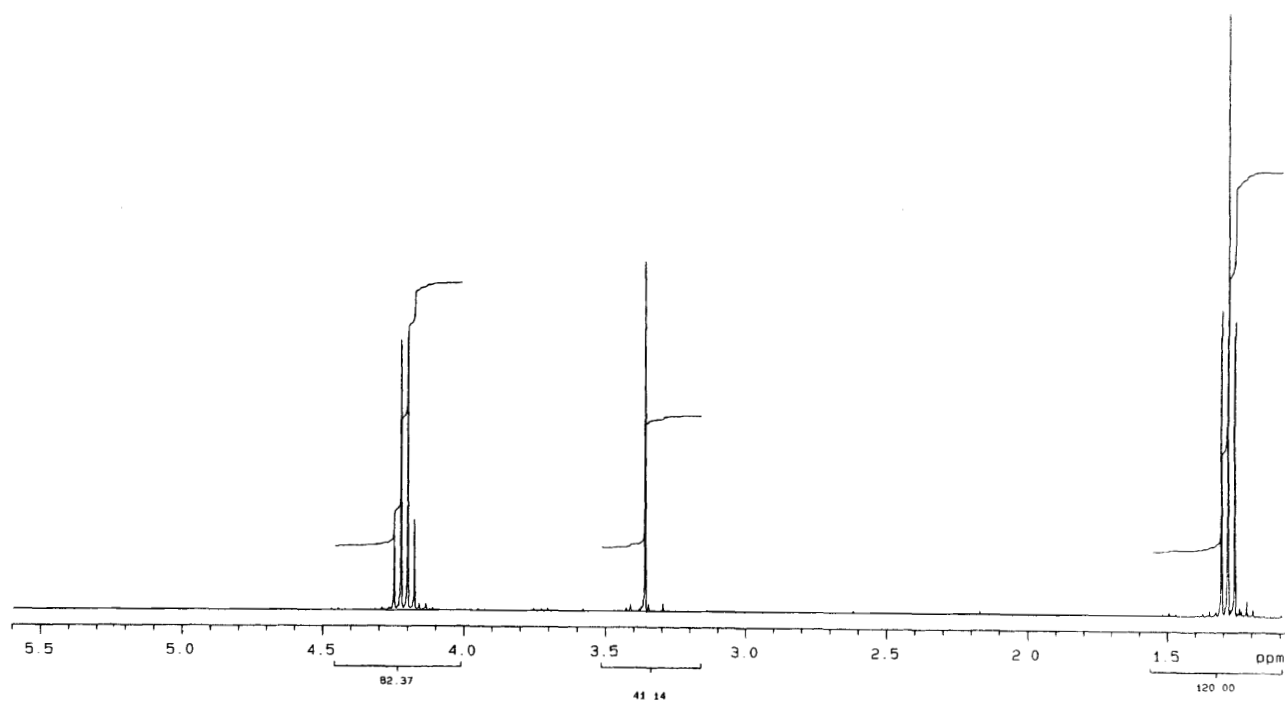
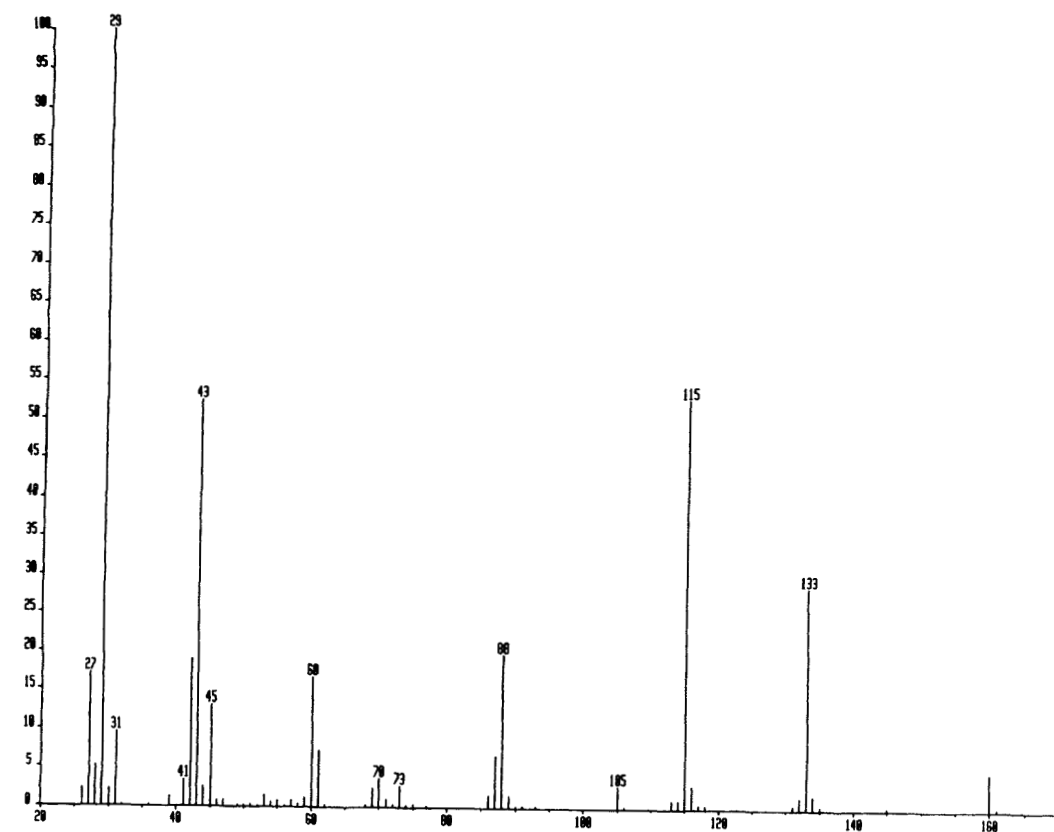
Sample 11.4



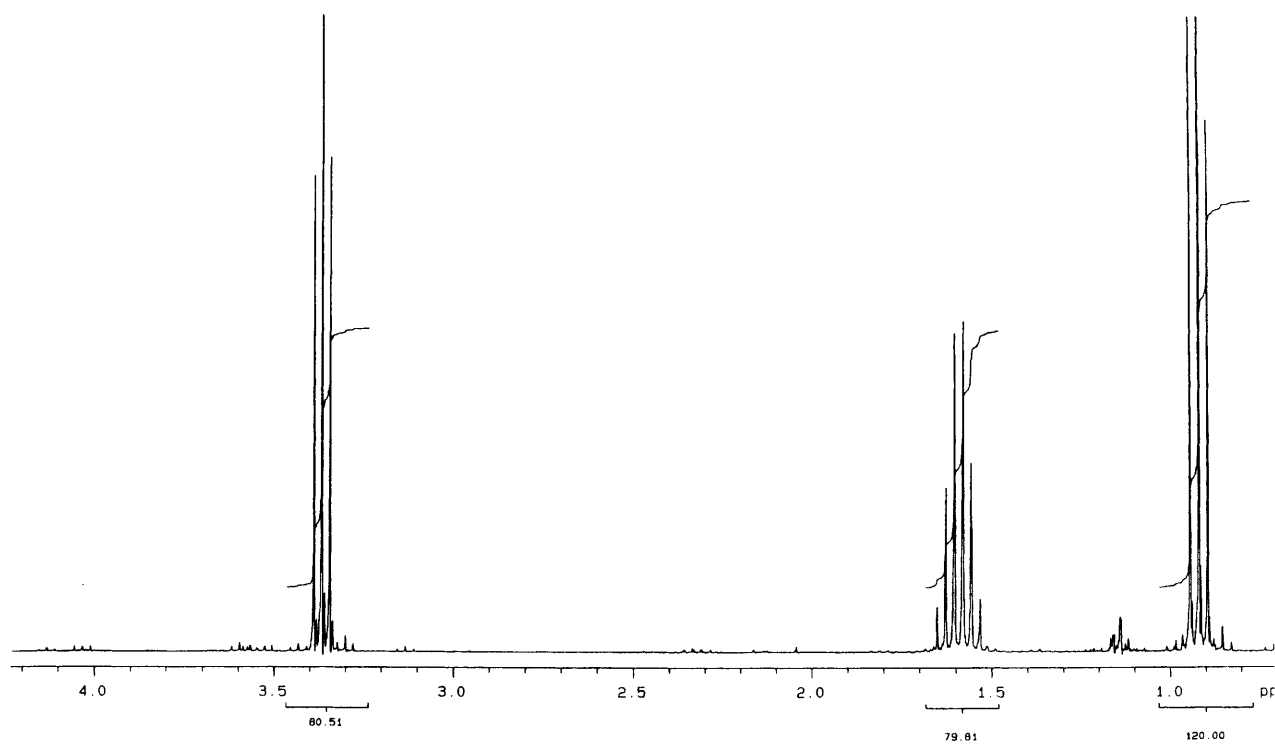
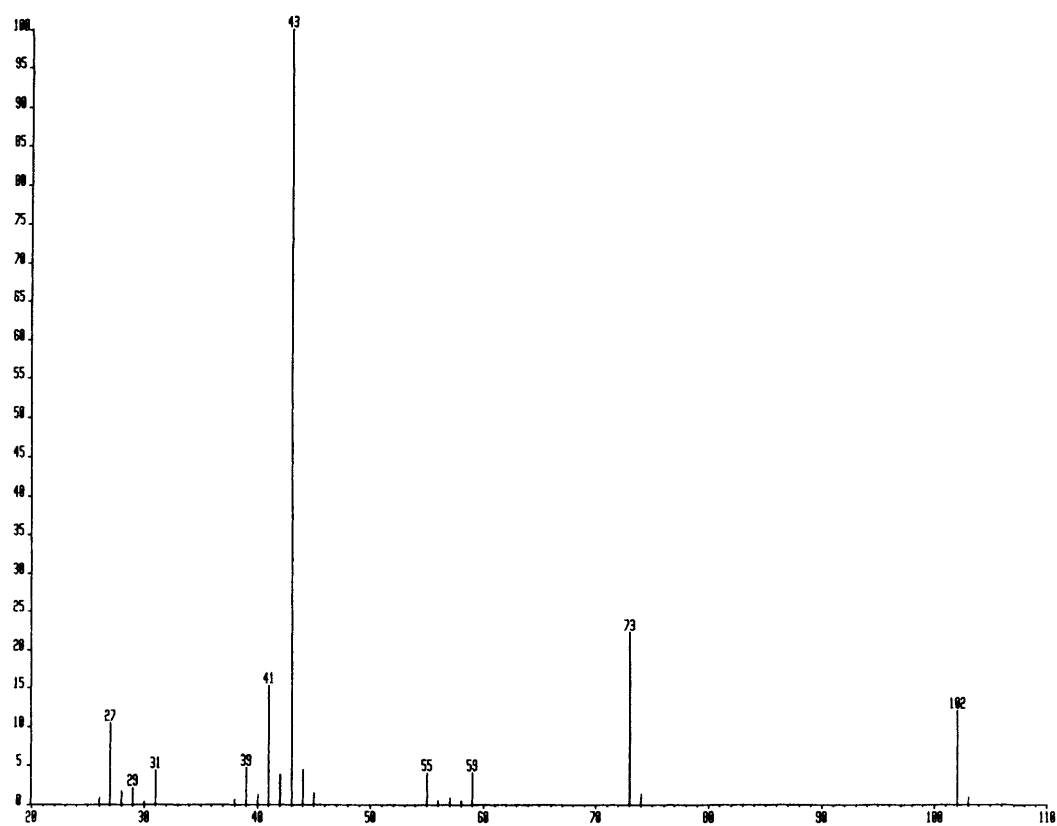
Sample 11.5



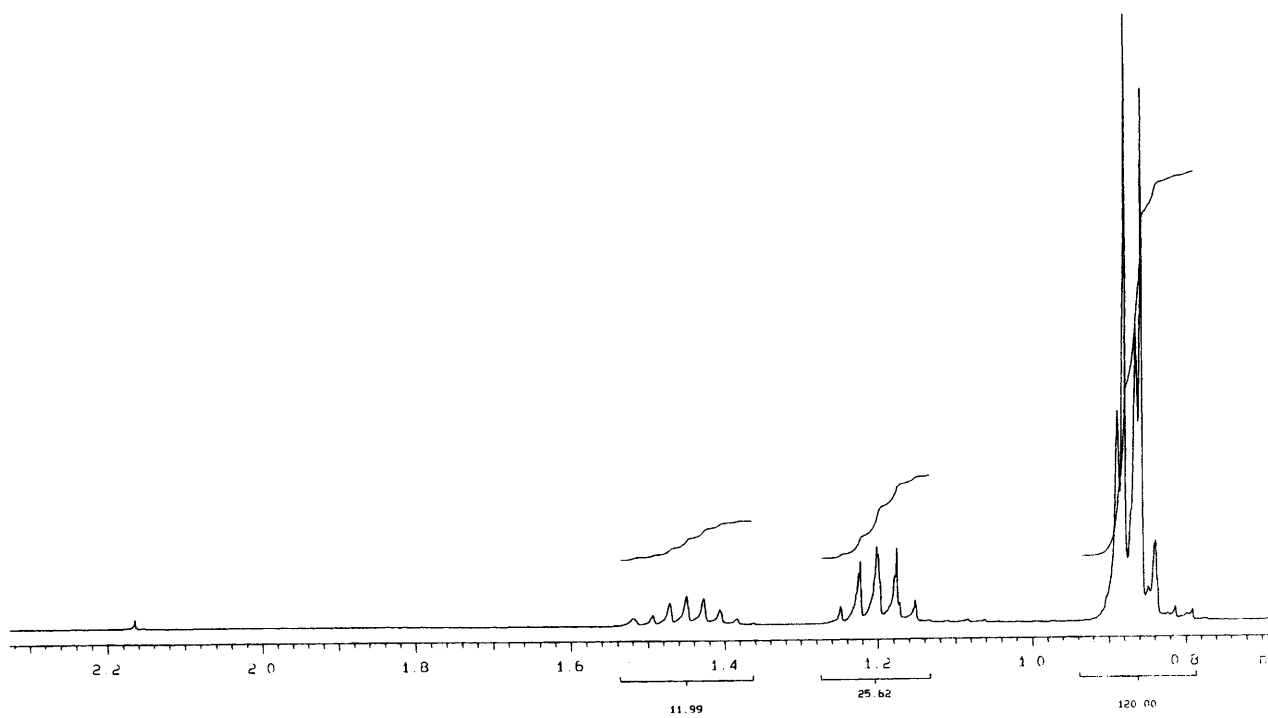
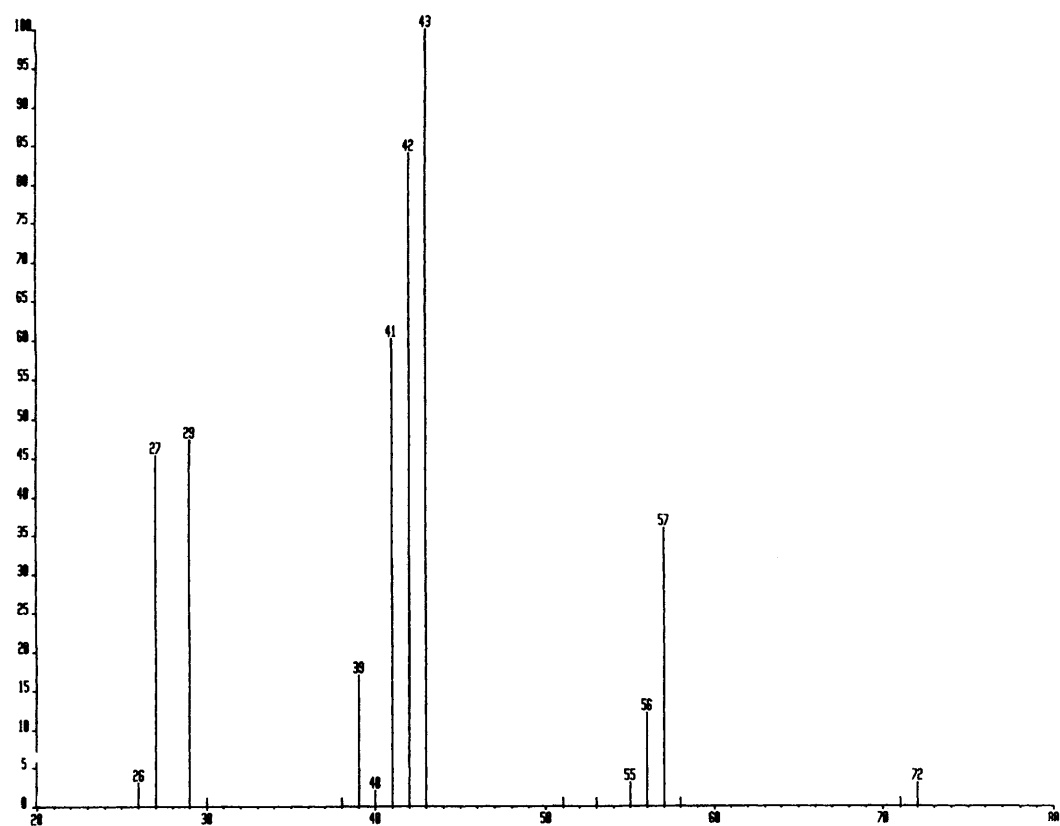
Sample 11.6



Sample 11.7

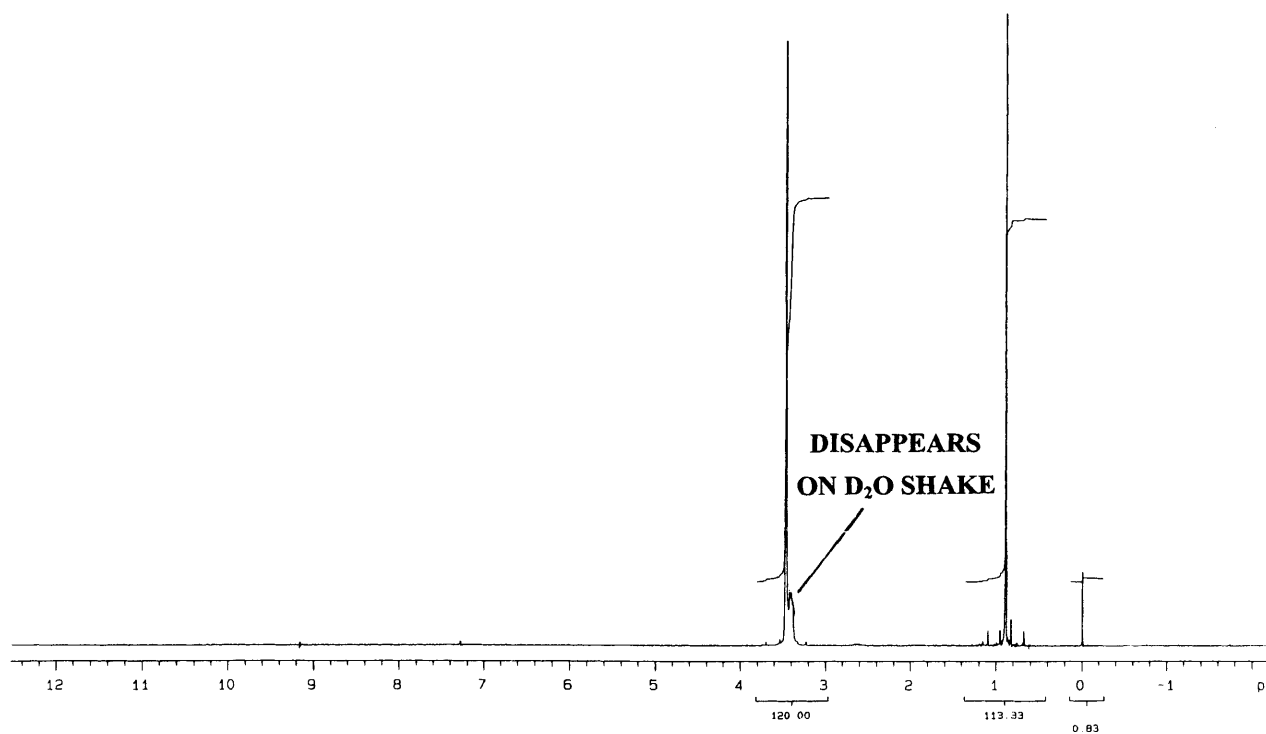
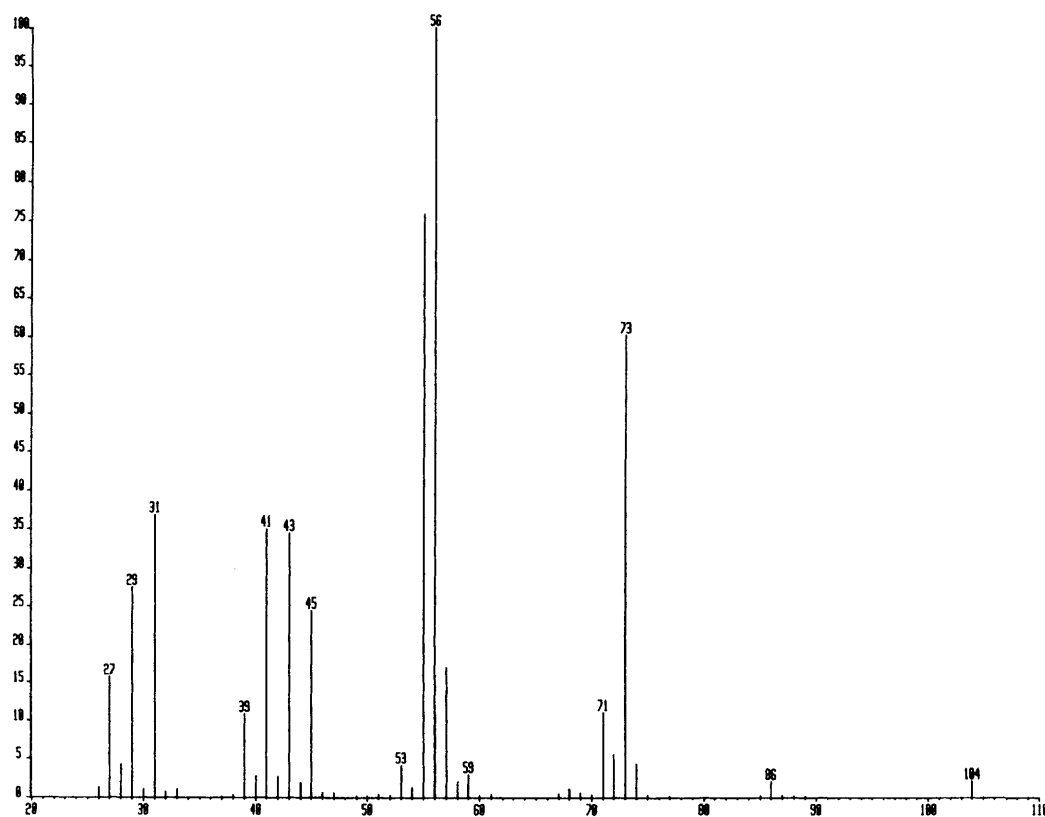


Sample 11.8



Sample 11.9





Sample 11.10

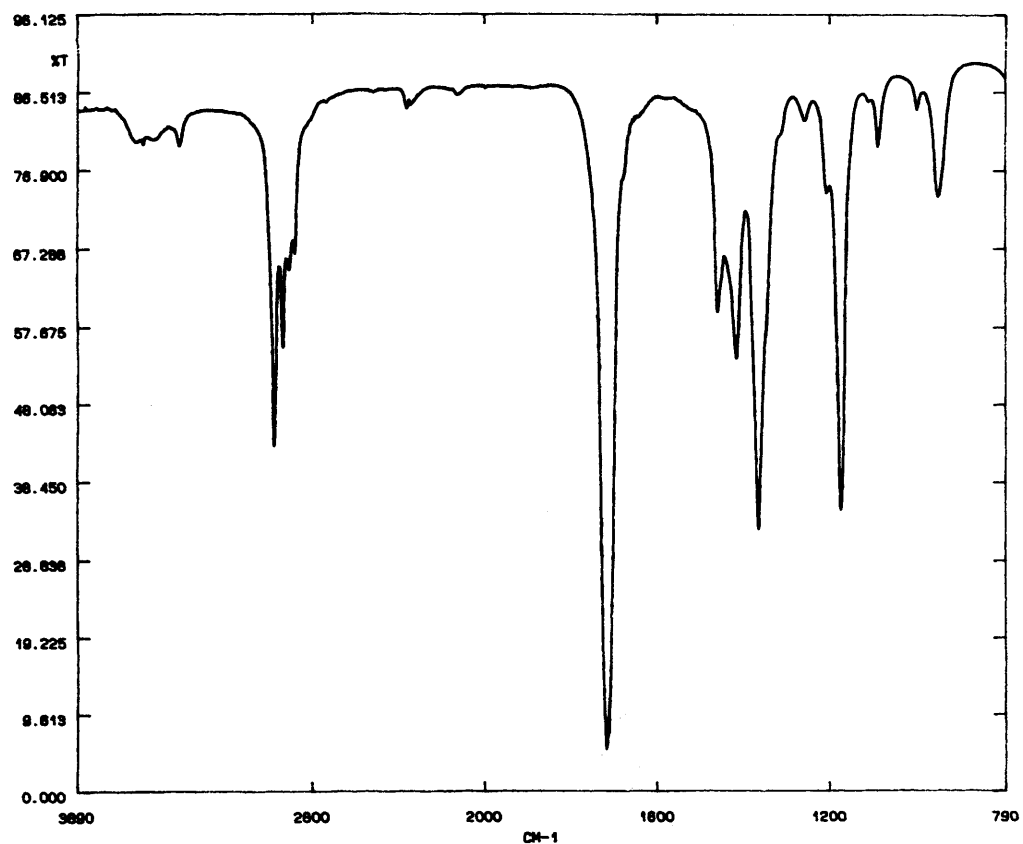


## **Problems in Interpreting Infrared Spectra, Mass Spectra, Ultraviolet Spectra, $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra and $^1\text{H}$ Nuclear Magnetic Resonance Spectra**

In this chapter we bring all the techniques together, which gives us the ability to identify thousands of simple molecules. However, it also brings the problem of putting together data from up to five techniques to identify a molecule. It is best to start with the infrared spectrum, and to determine the functional groups. Next, the mass spectrum will identify the halogens, reveal the molecular weight and often give us useful structural information. The ultraviolet spectrum can tell us about conjugation in a molecule. In many cases, we can then identify the molecule from the  $^{13}\text{C}$  NMR spectrum, but then we must always check that our solution is consistent with the  $^1\text{H}$  NMR spectrum. In other cases, the  $^{13}\text{C}$  NMR spectrum will not provide sufficient information to give complete identification, and the  $^1\text{H}$  NMR is vital. It is necessary to look back at data obtained—for example, if you missed a fully substituted double bond in the infrared, which is easy to do as the peak is very small, then it would be revealed by the  $^{13}\text{C}$  spectrum; you may then have to modify your views on the significance of a carbonyl peak frequency.

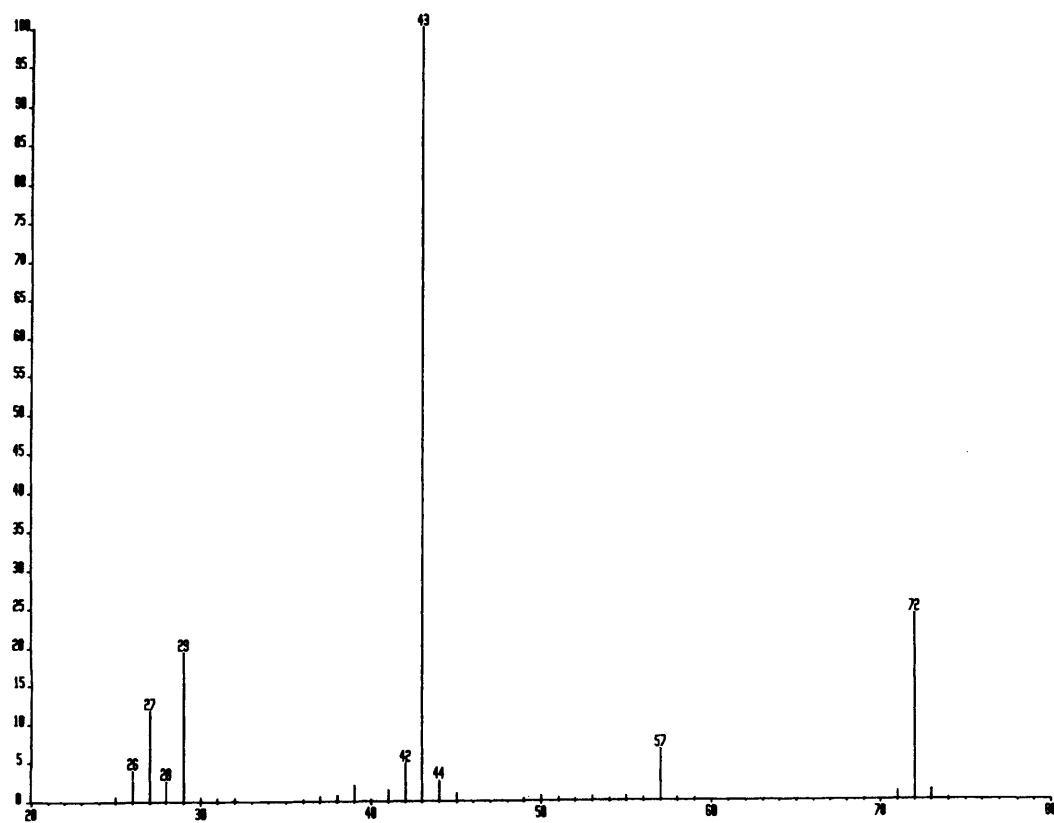
It is often difficult to identify alicyclic molecules by  $^1\text{H}$  NMR, as the spectra become very complicated in rigid systems, but these molecules are relatively easy to identify by  $^{13}\text{C}$  NMR. Always consider the symmetry of a molecule—it can often be used to distinguish between possibilities, particularly when considering  $^{13}\text{C}$  spectra.

This exercise is the final test of your ability to bring together the data from all techniques. In each case you are given the infrared, mass,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra and, where appropriate, the ultraviolet spectra. You should be able to identify all the samples from the data provided.

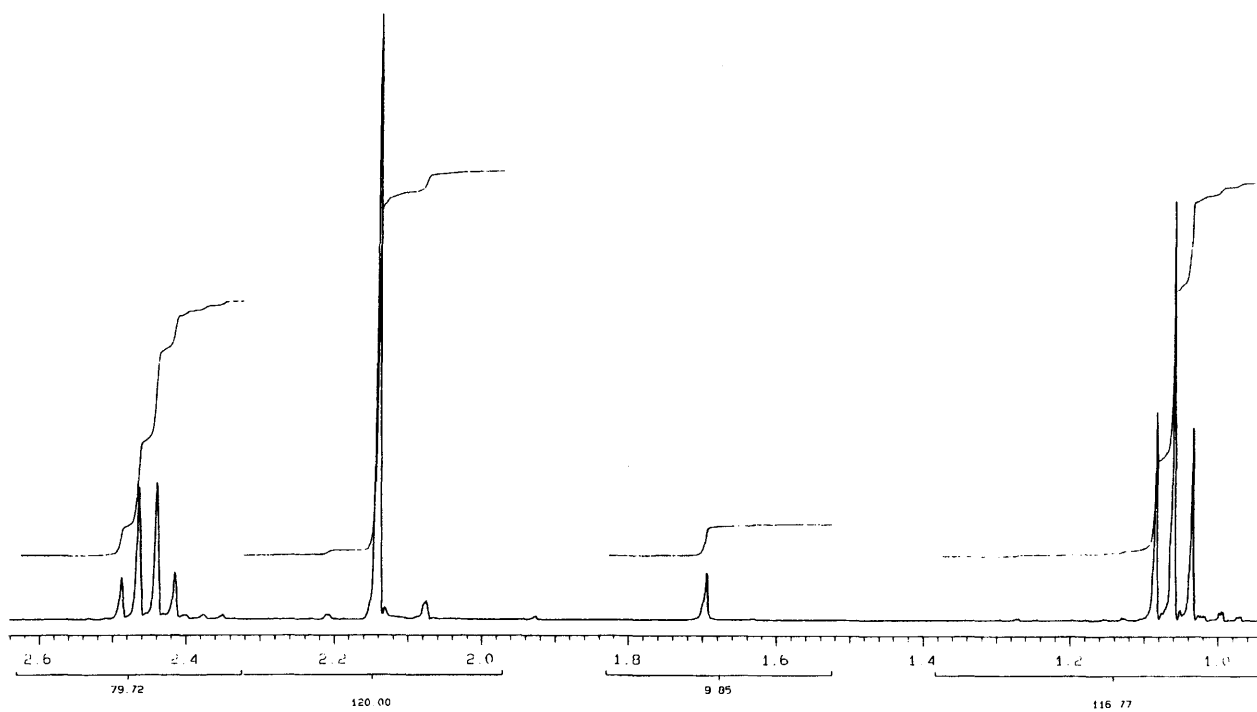
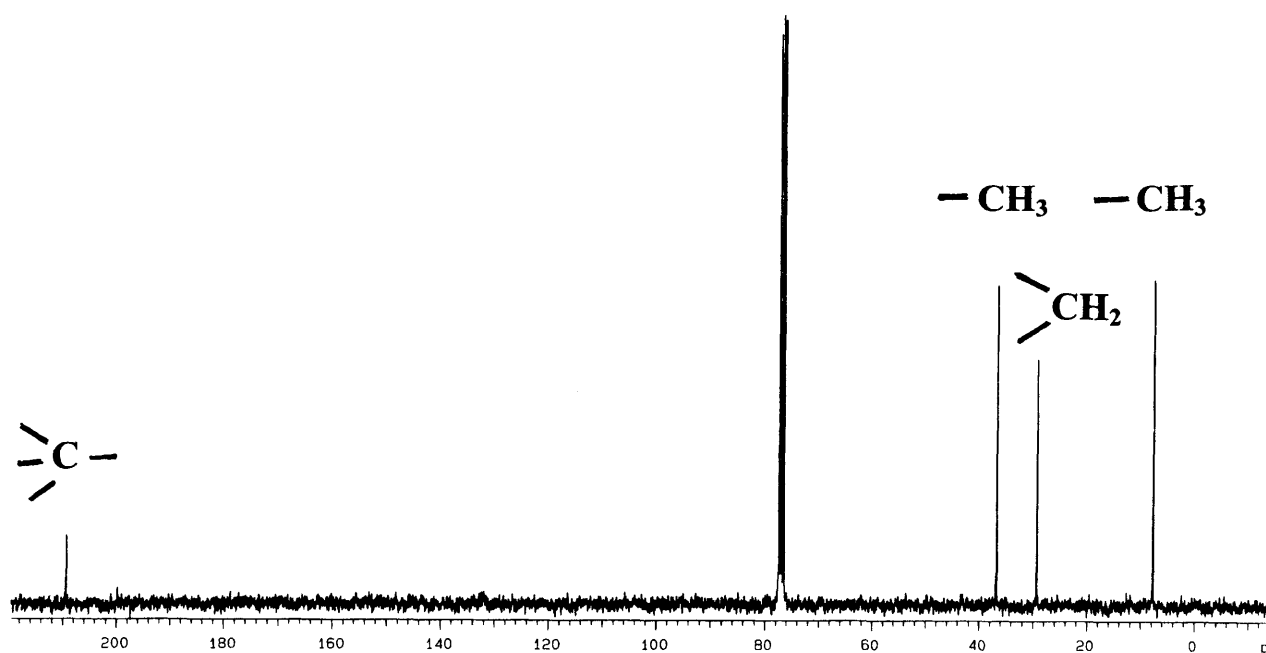


PEAK THRESHOLD = 0.96 XT

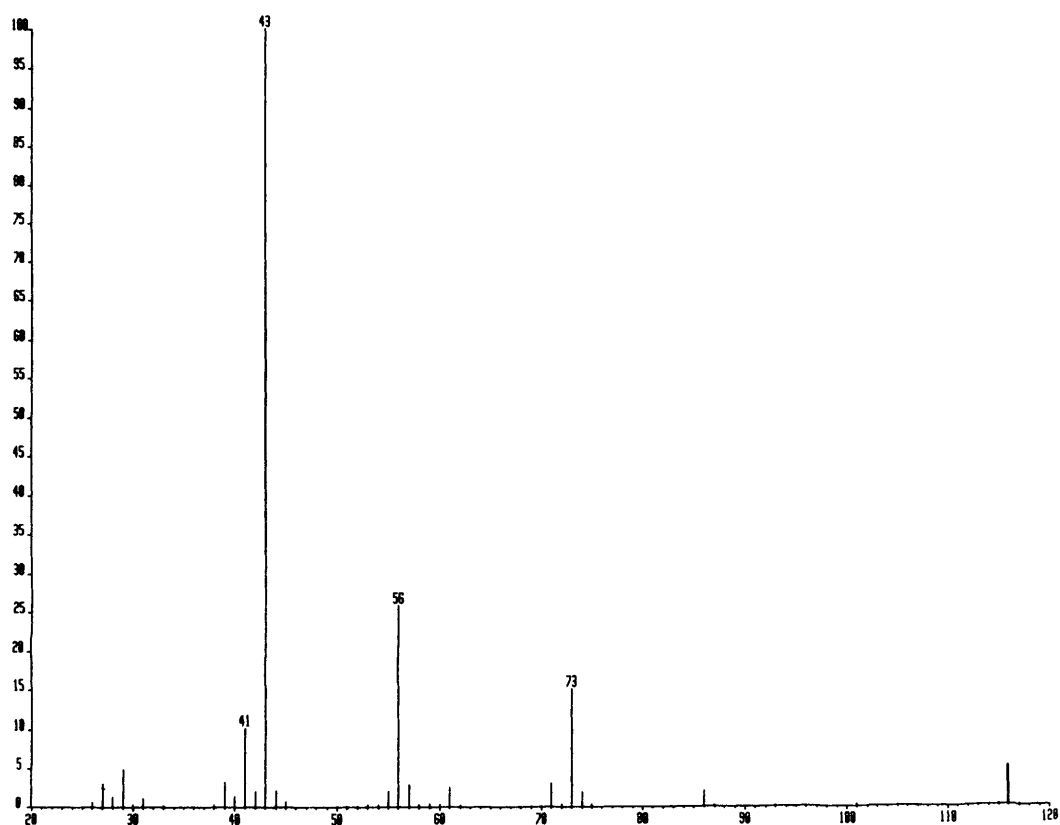
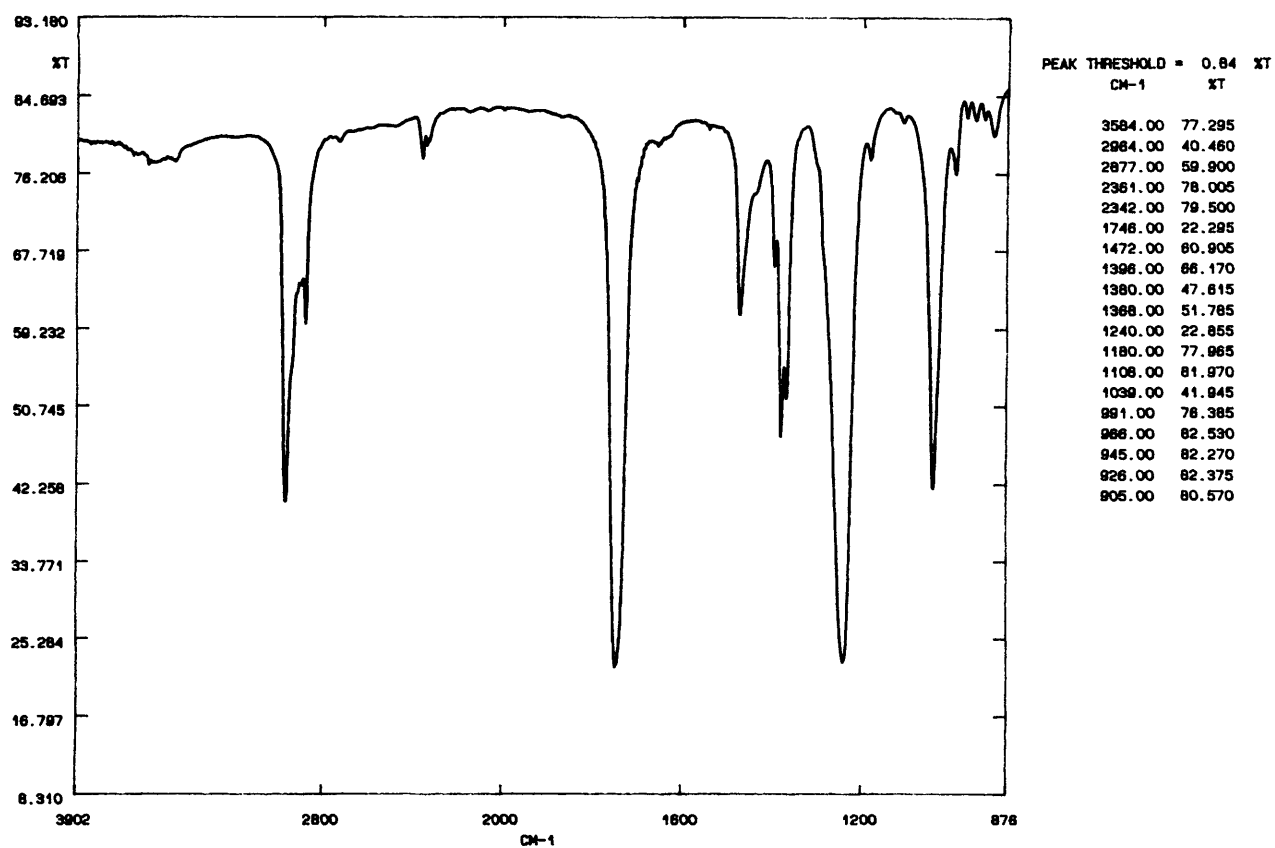
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3416.00	79.970
2980.00	43.075
2940.00	55.345
2910.00	64.900
2883.00	66.895
2360.00	84.670
2123.00	86.415
1718.00	5.410
1461.00	59.675
1417.00	53.885
1366.00	32.830
1258.00	83.180
1208.00	74.245
1173.00	35.205
1087.00	79.970
996.00	84.585
946.00	73.645



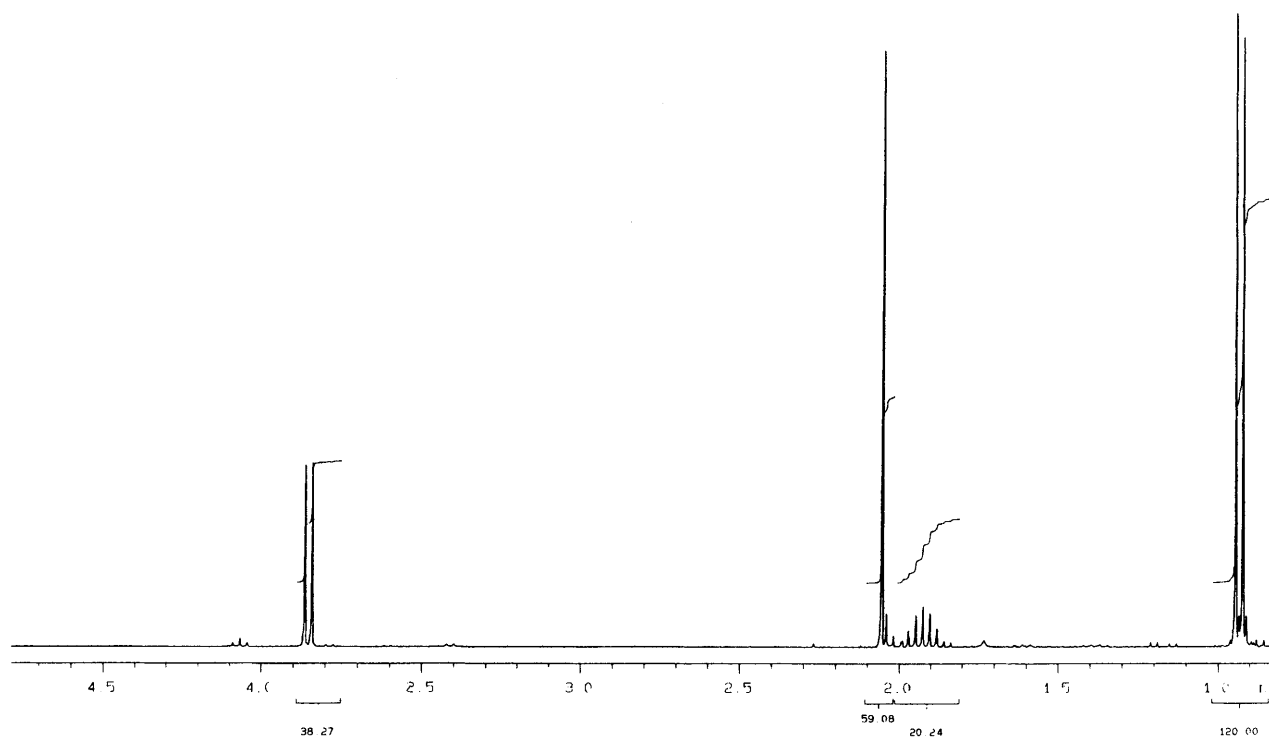
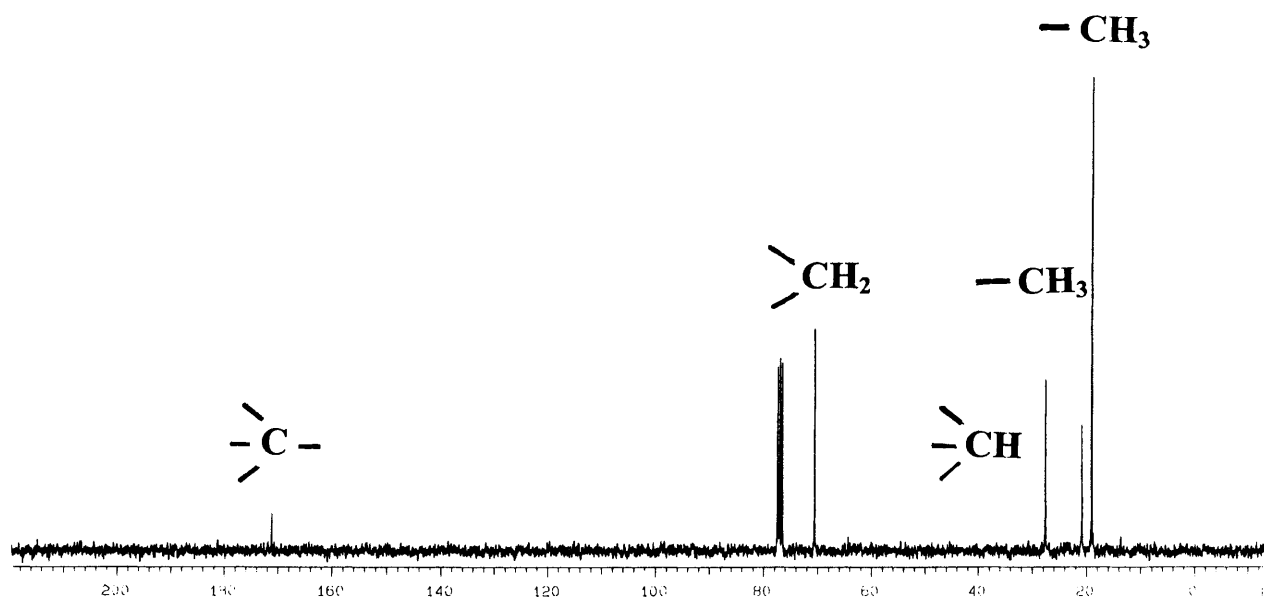
Sample 12.1



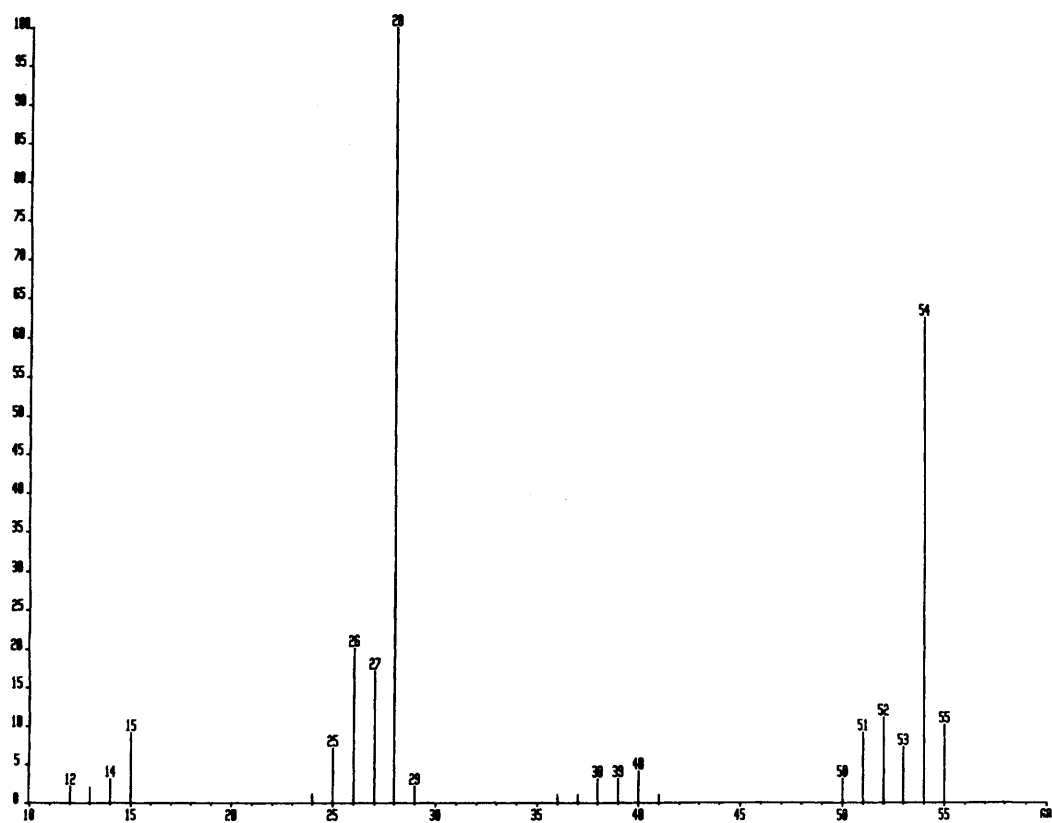
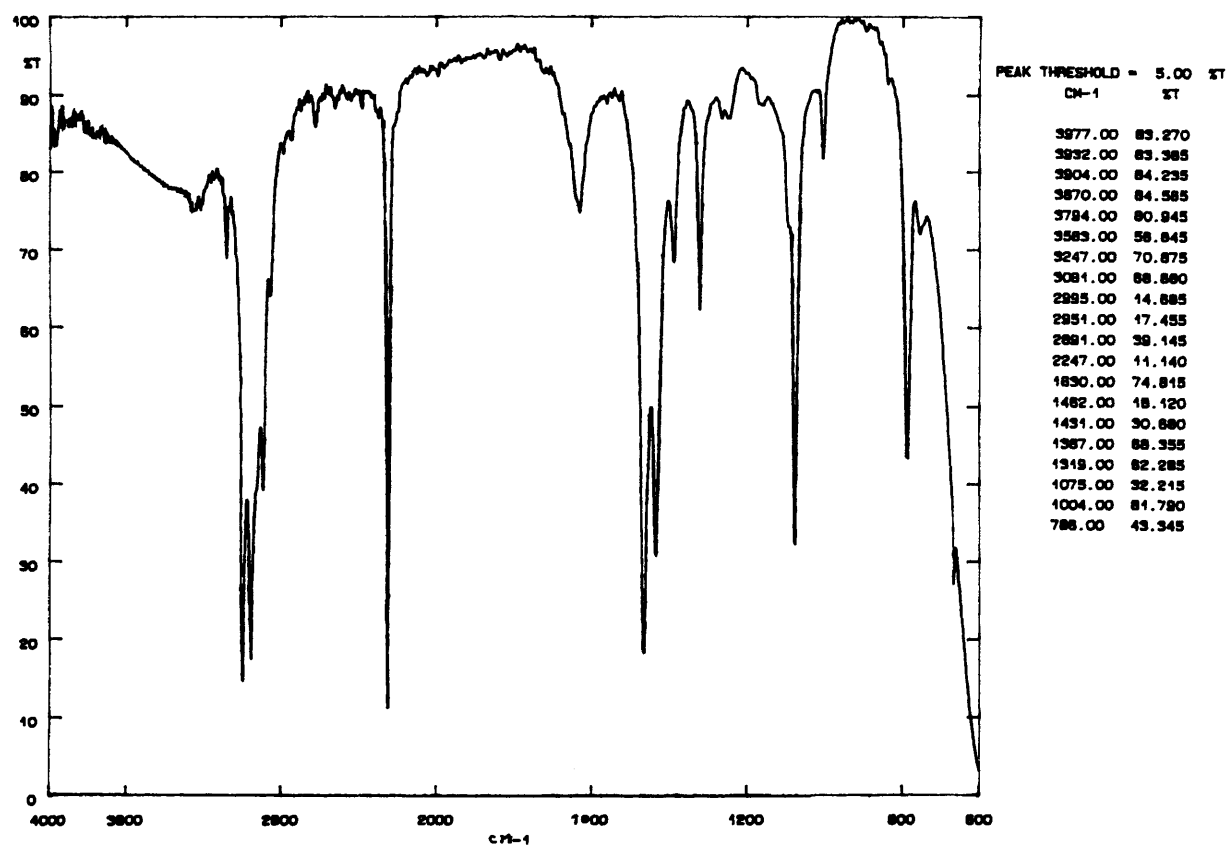
Sample 12.1 Continued



Sample 12.2

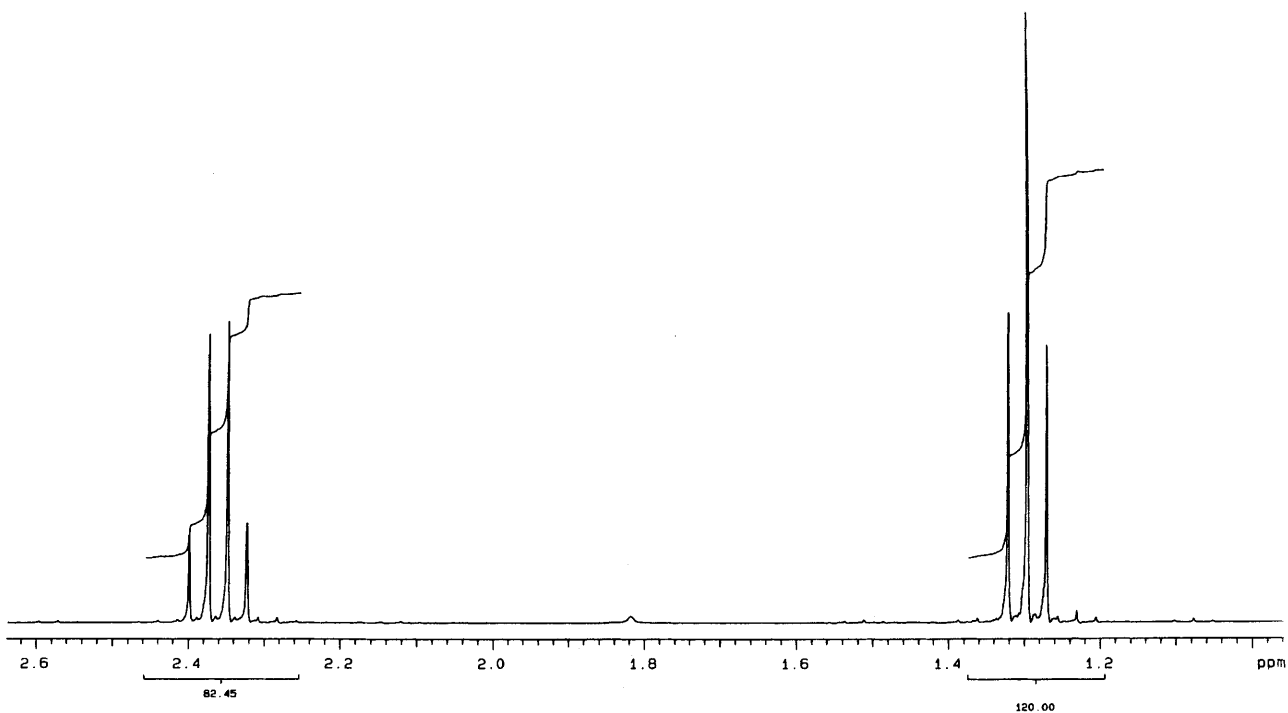
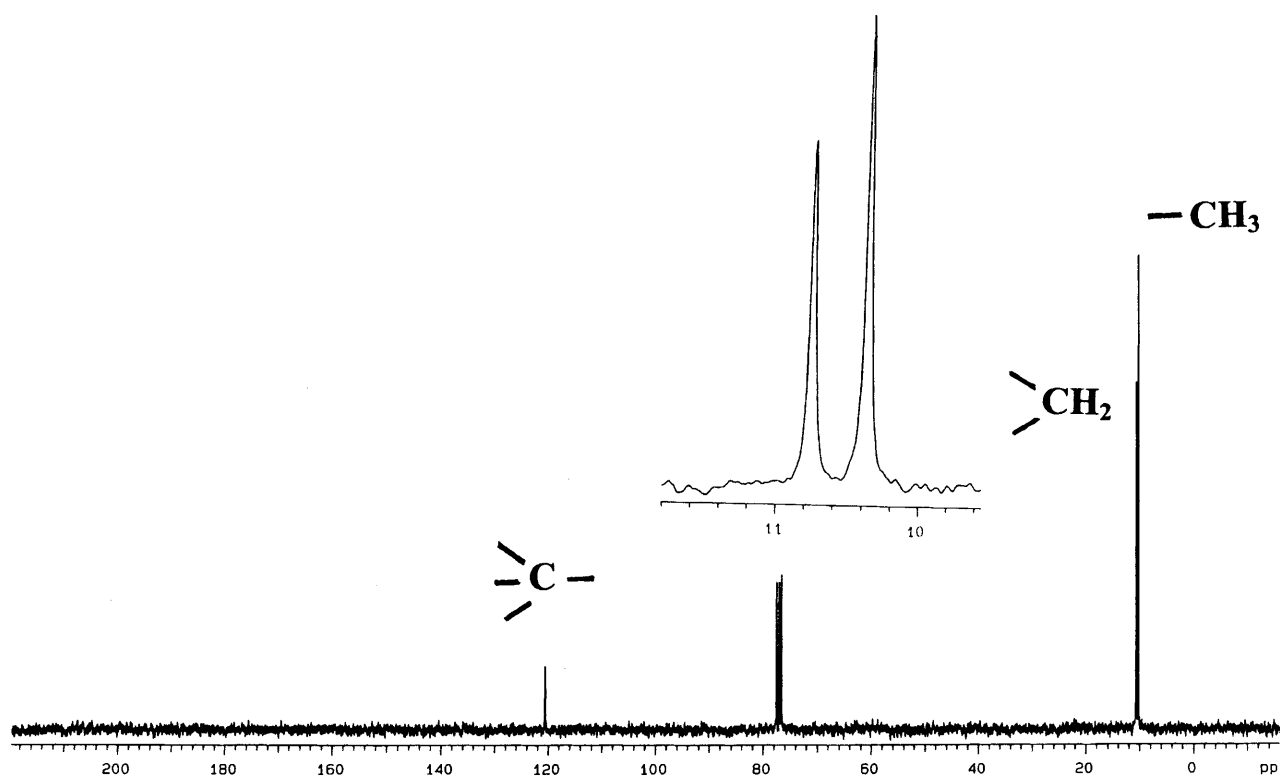


Sample 12.2 Continued

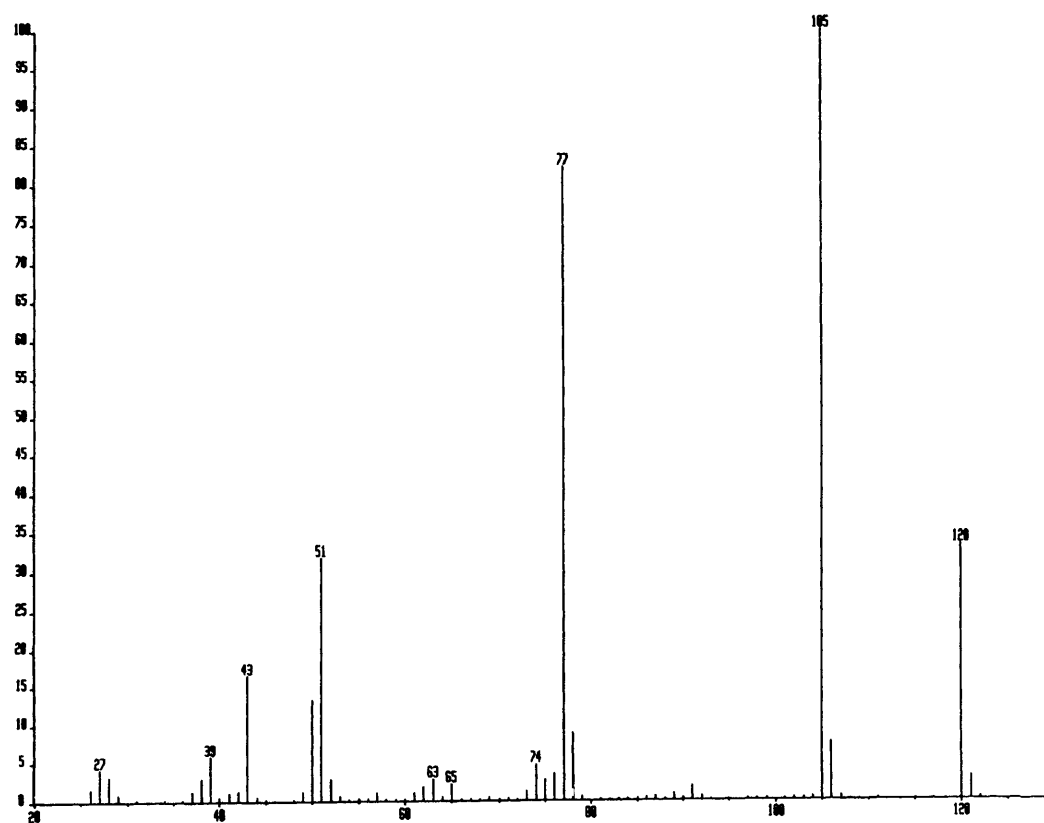
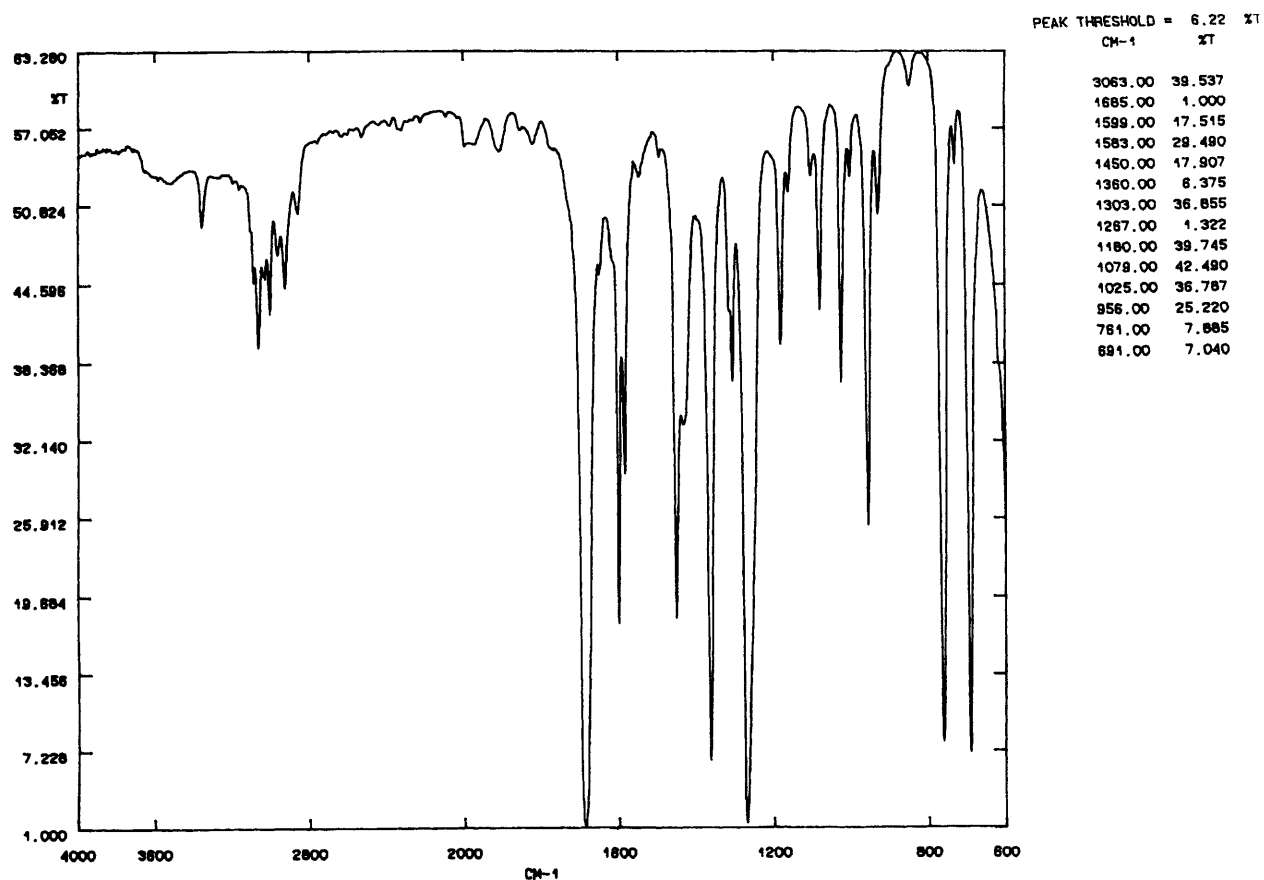


Sample 12.3

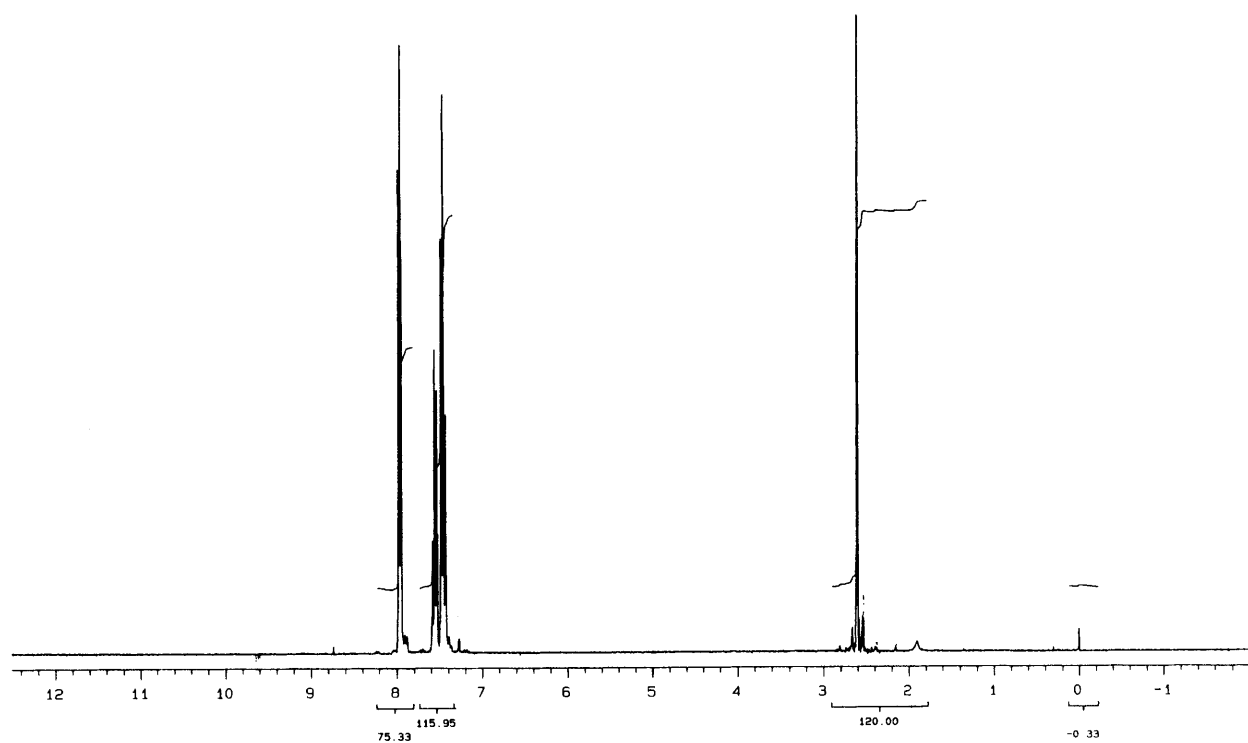
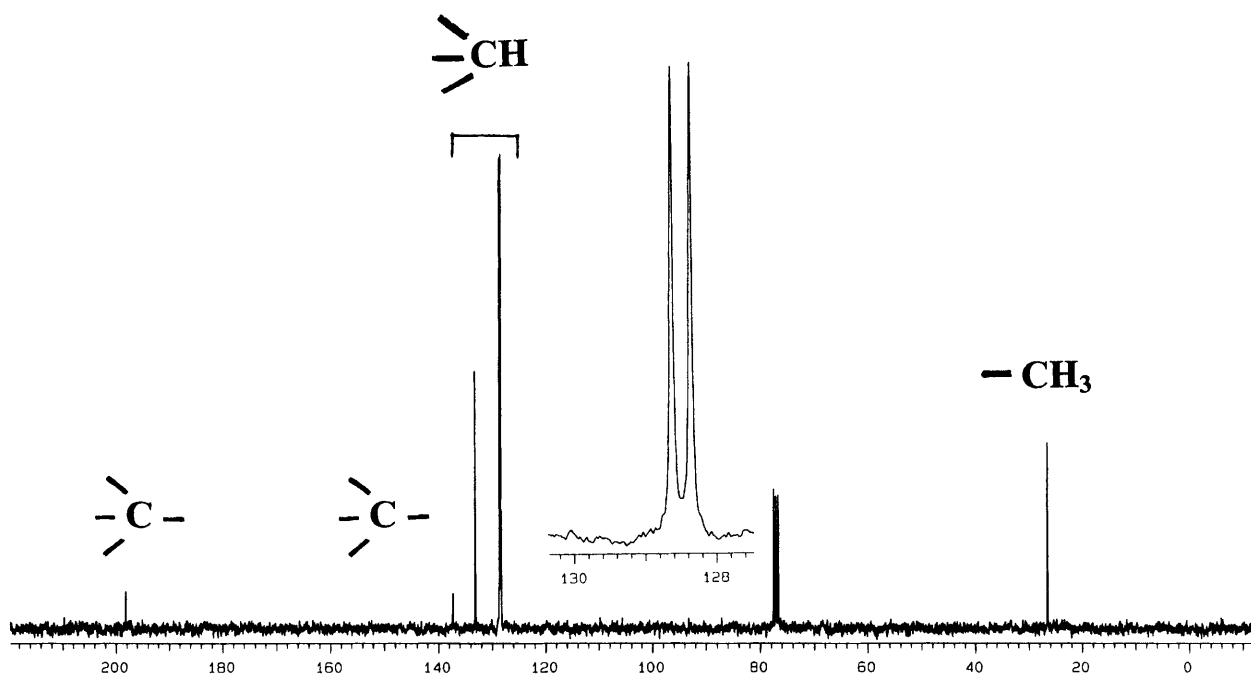




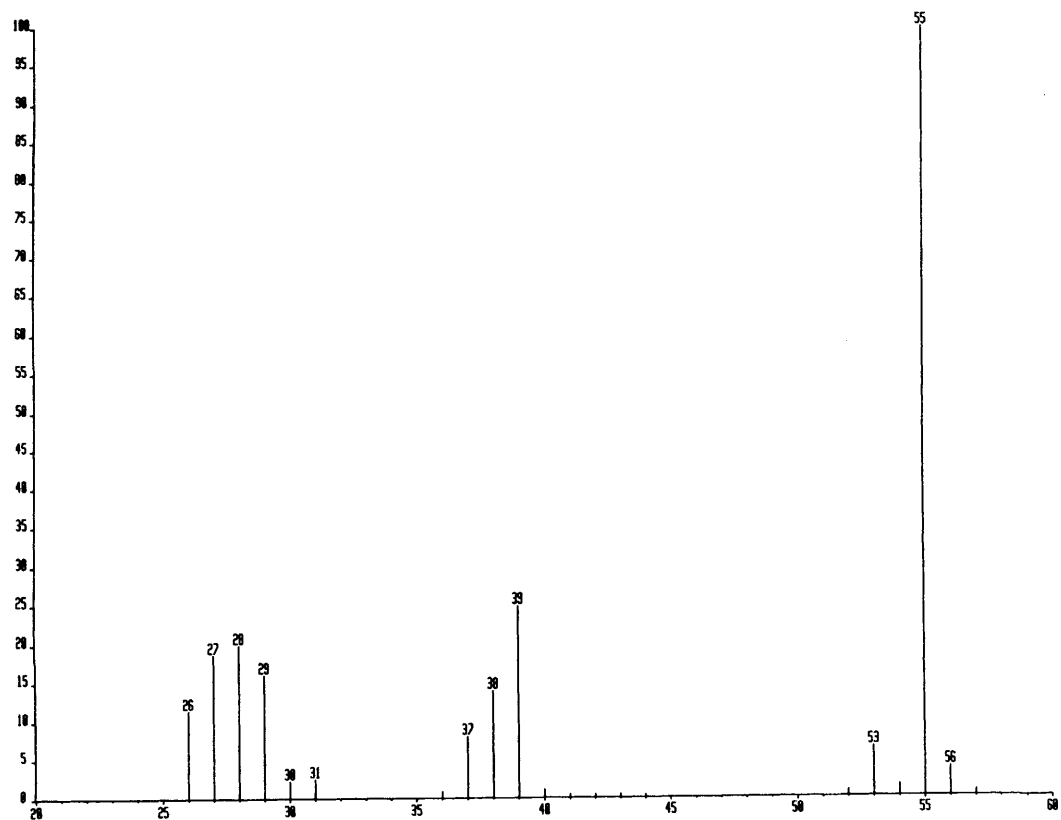
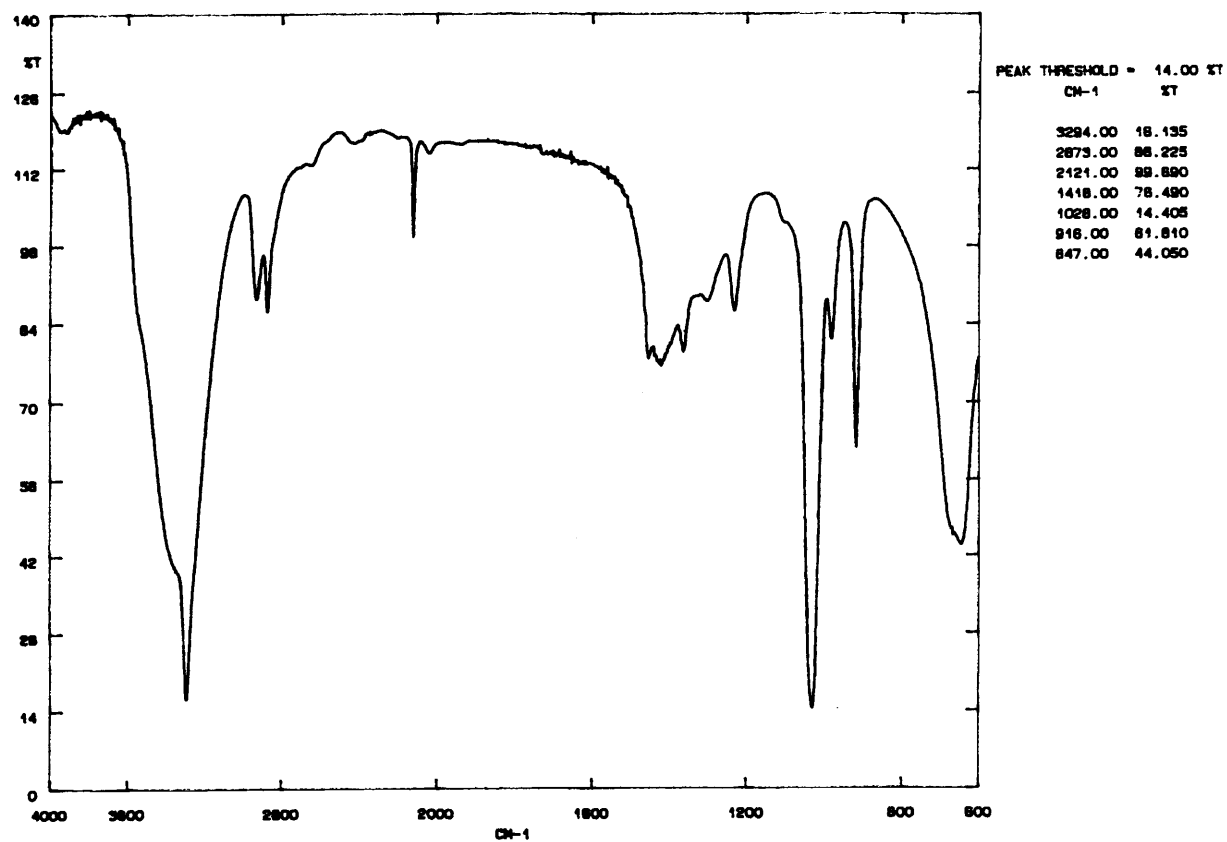
Sample 12.3 Continued



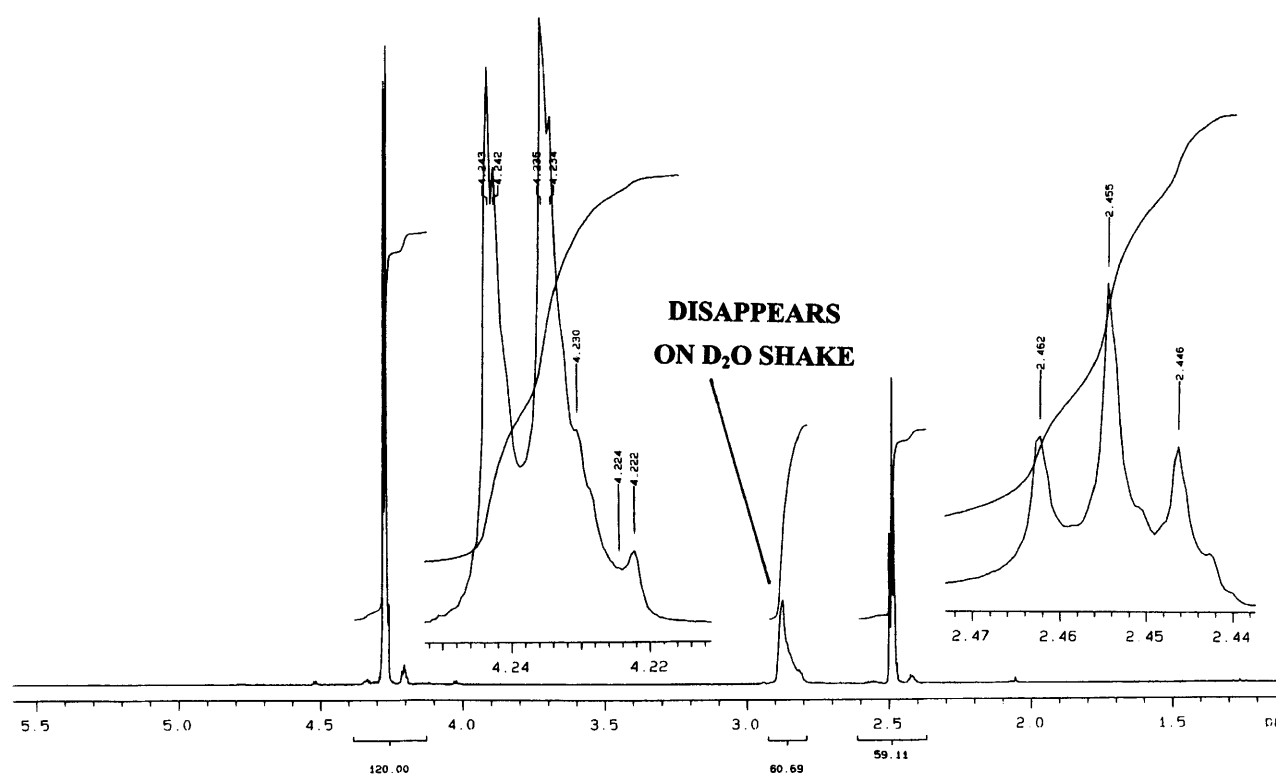
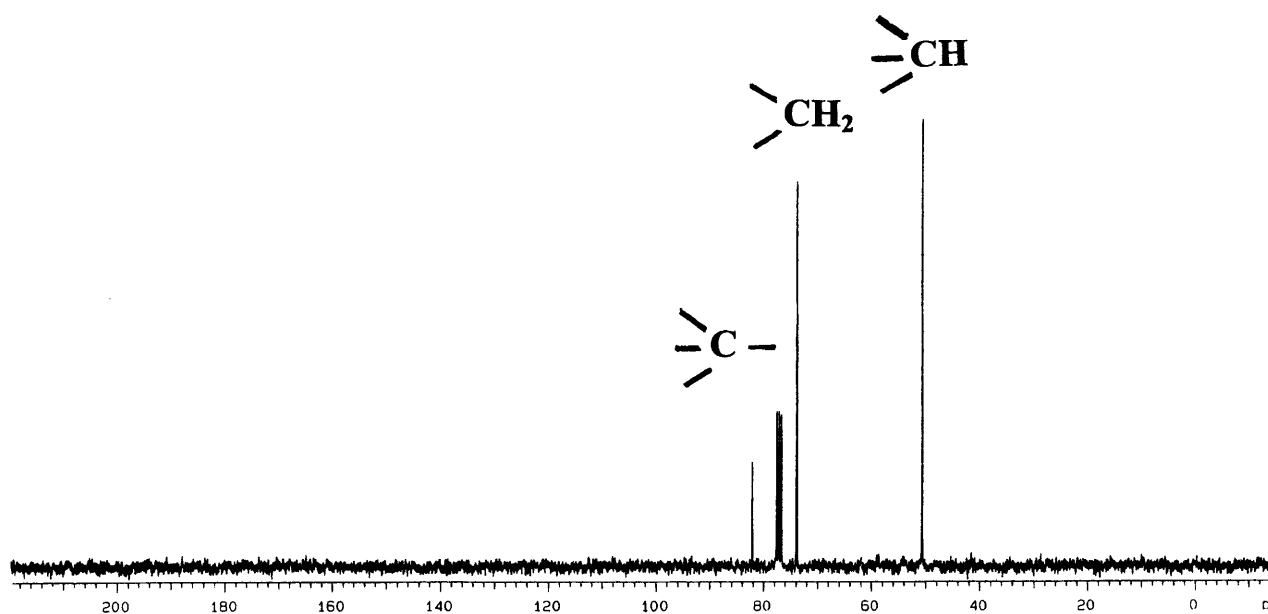
Sample 12.4



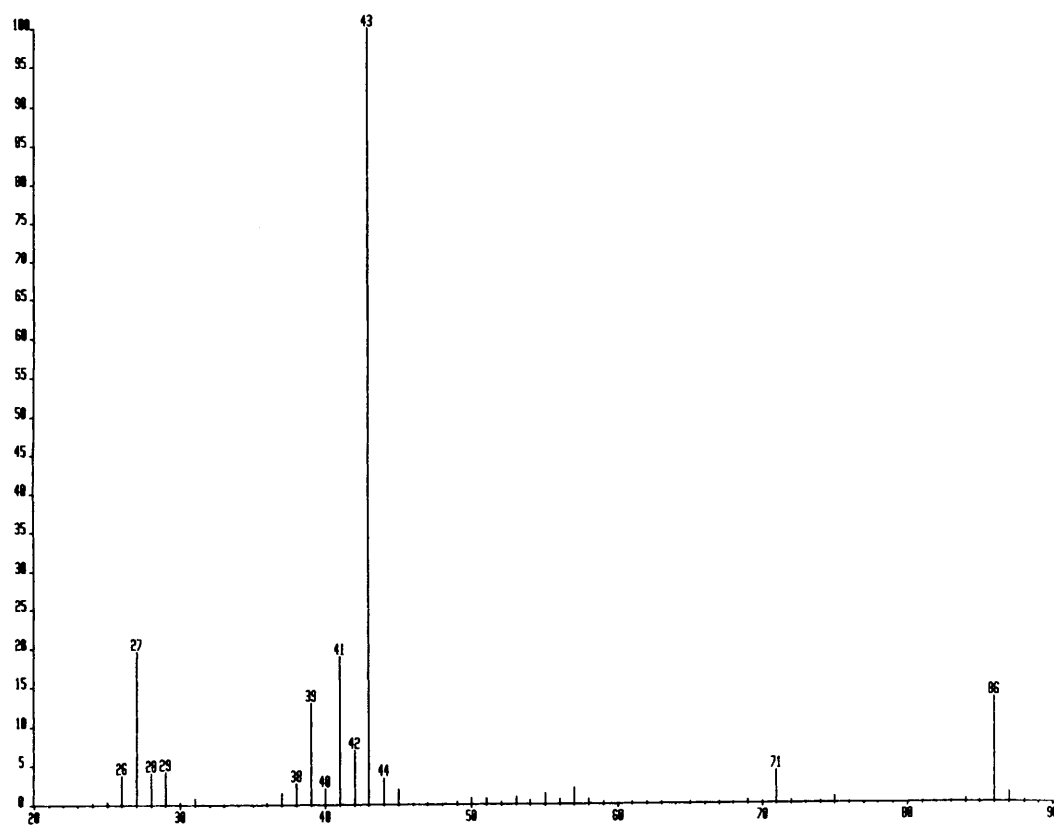
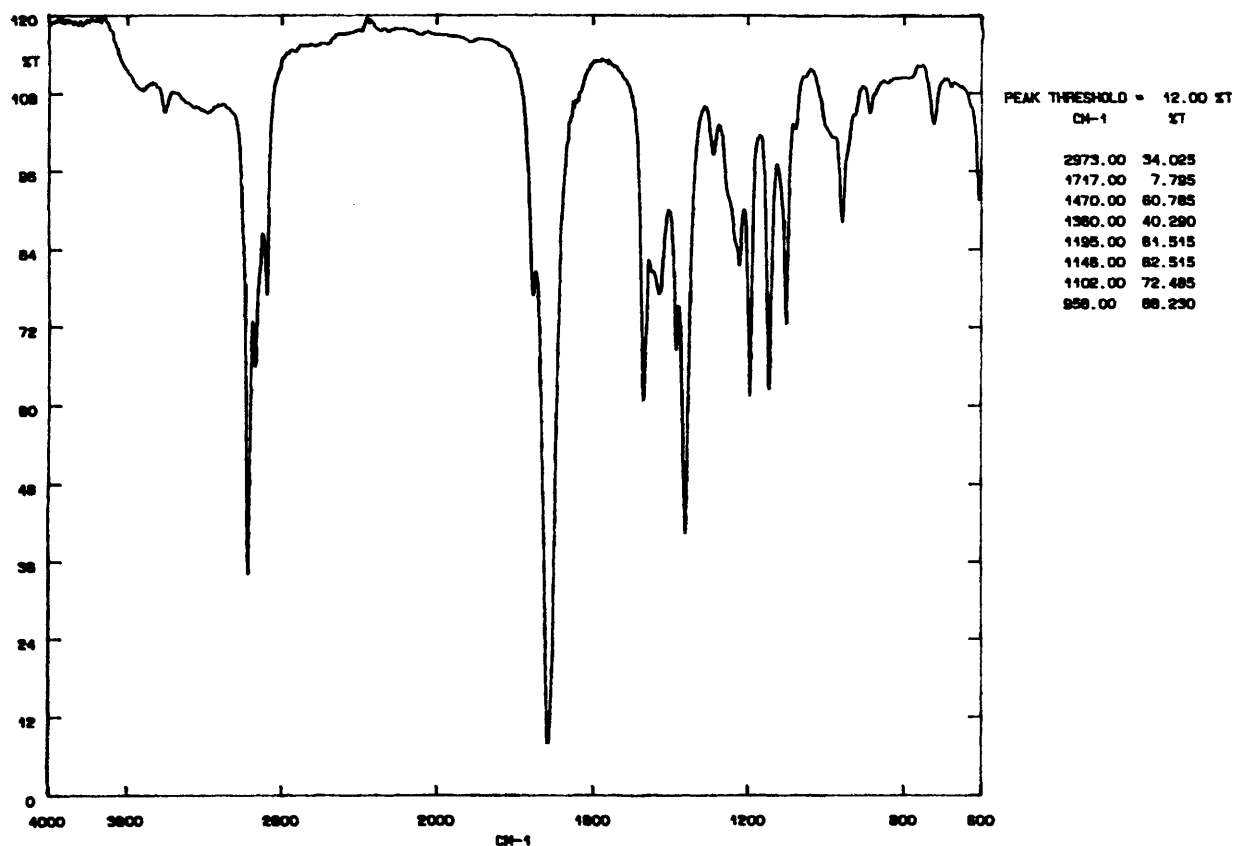
Sample 12.4 Continued



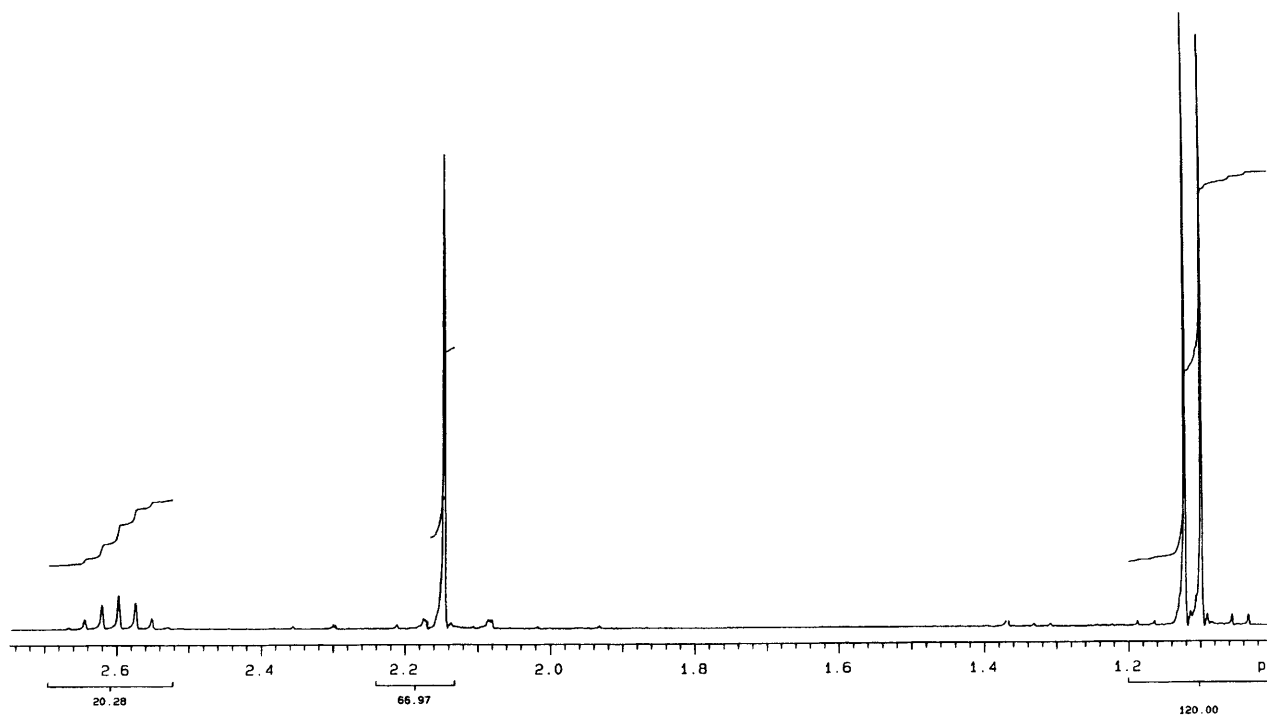
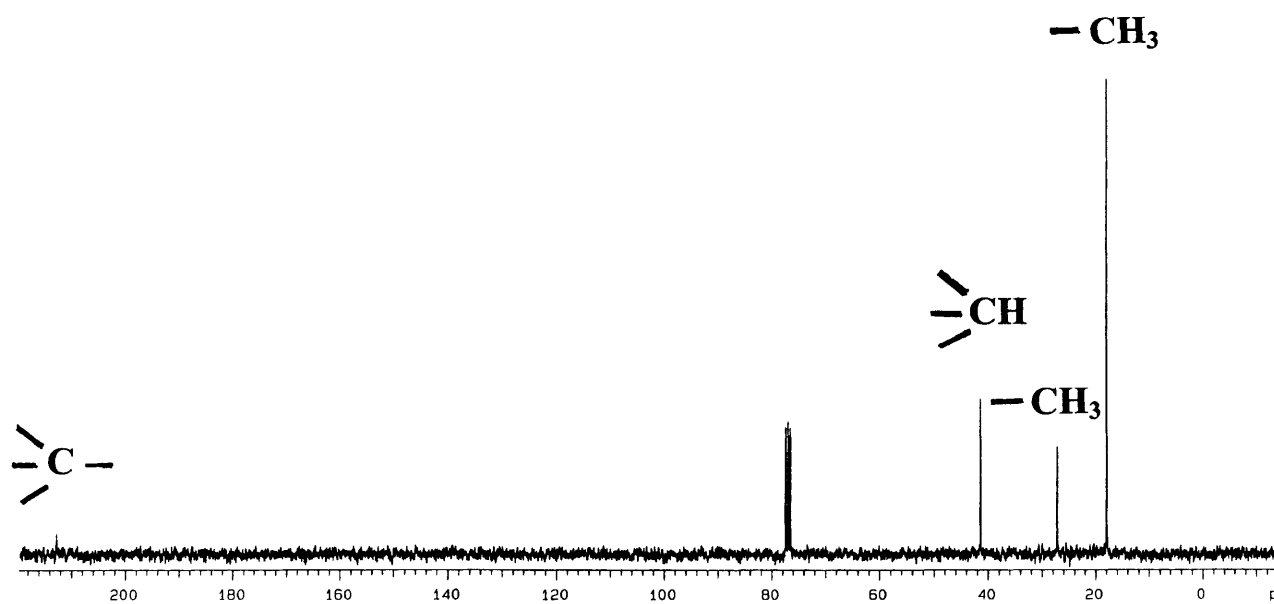
Sample 12.5



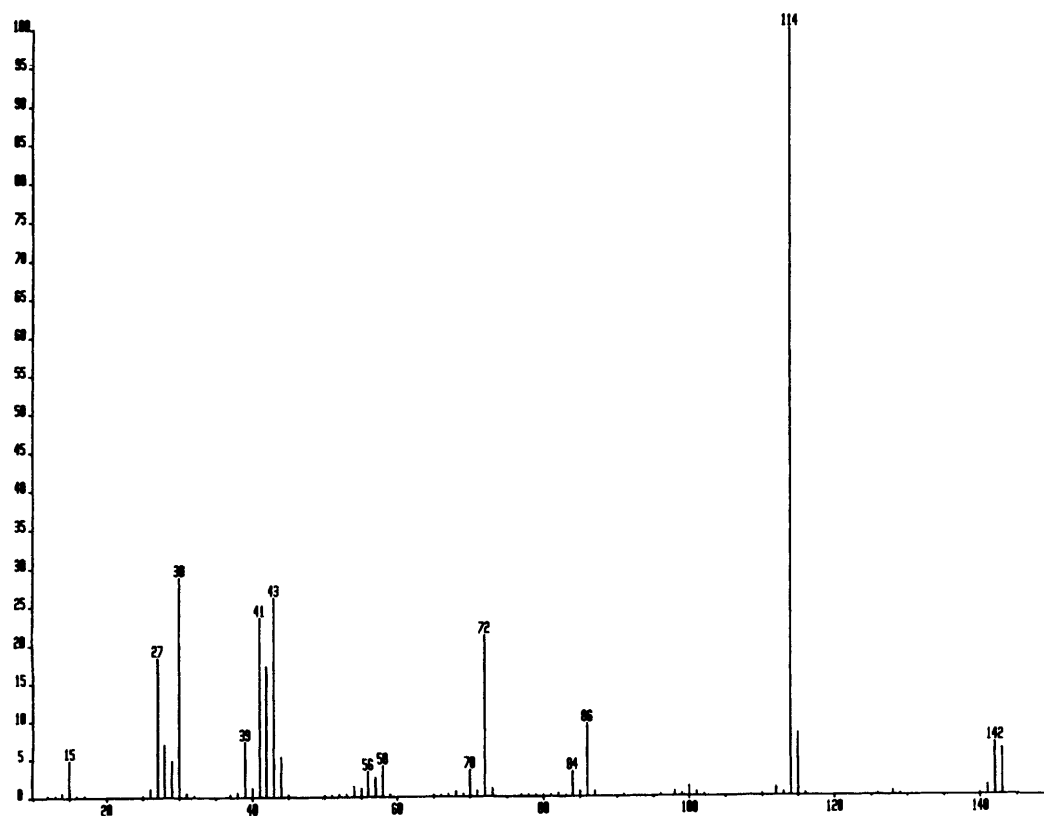
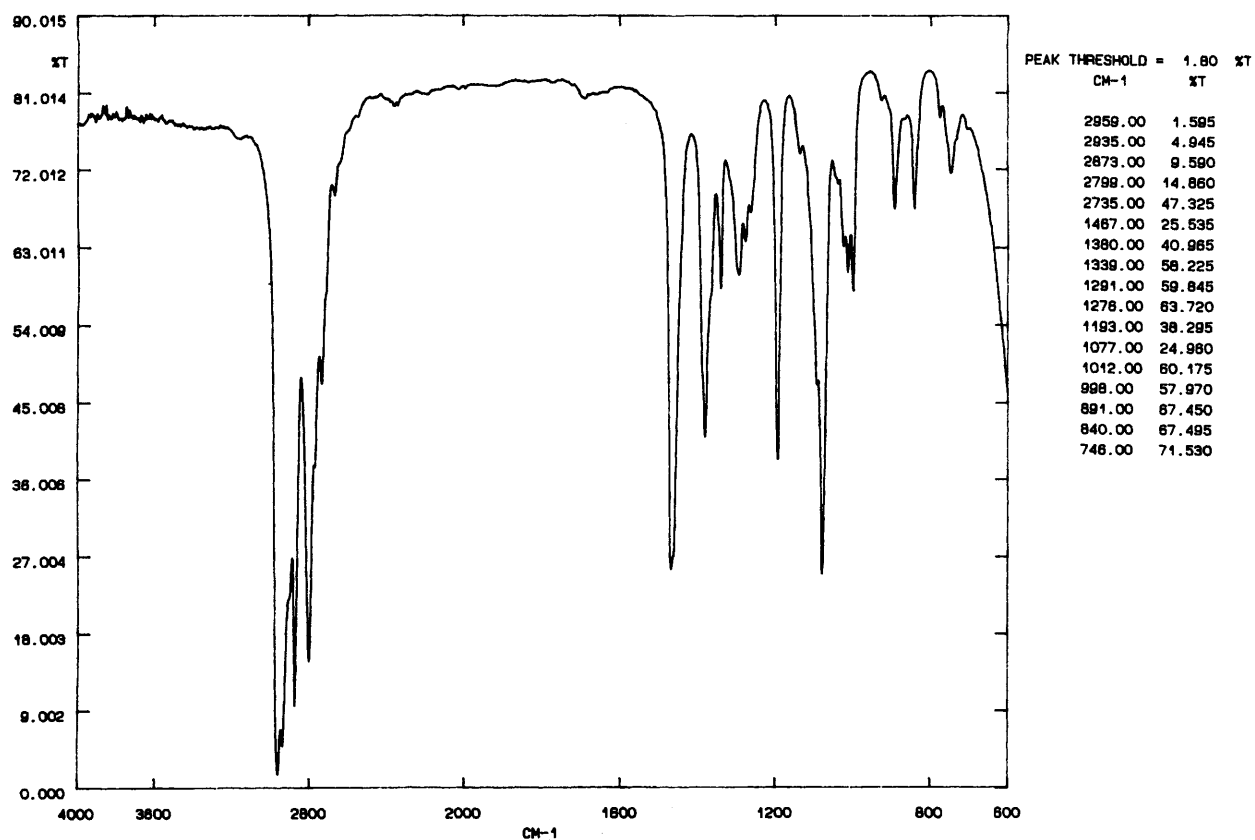
Sample 12.5 Continued



Sample 12.6

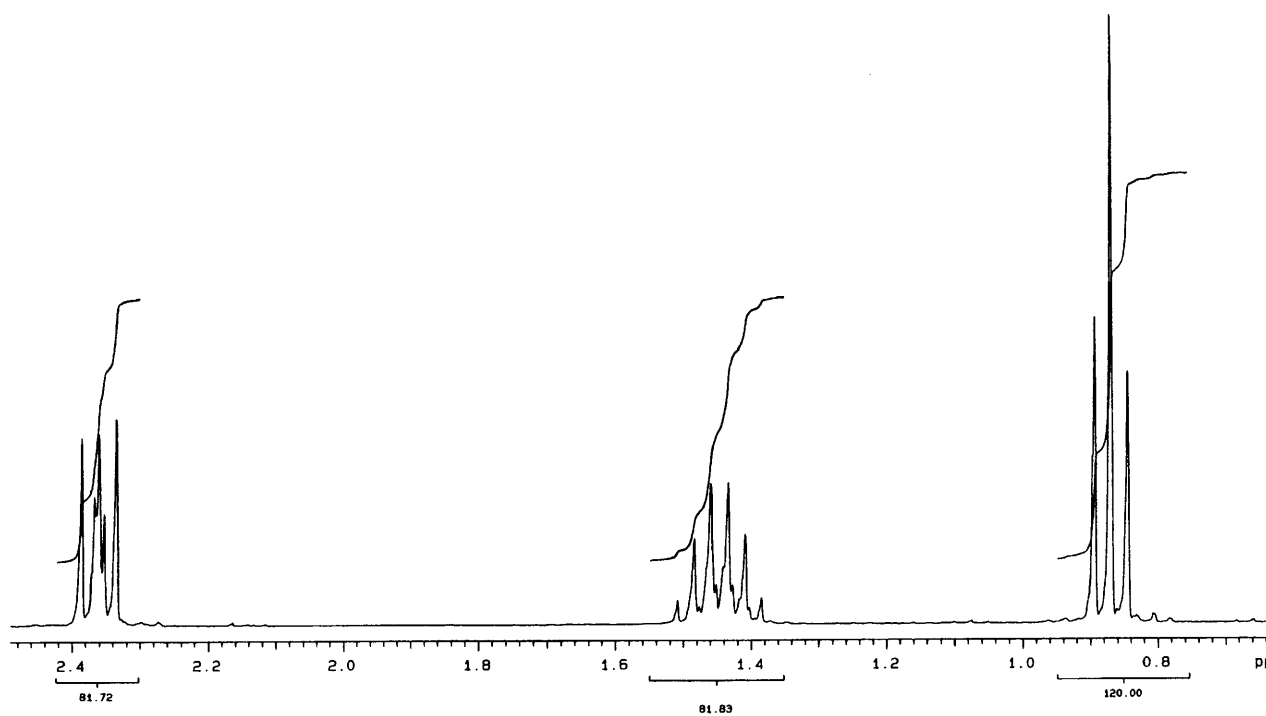
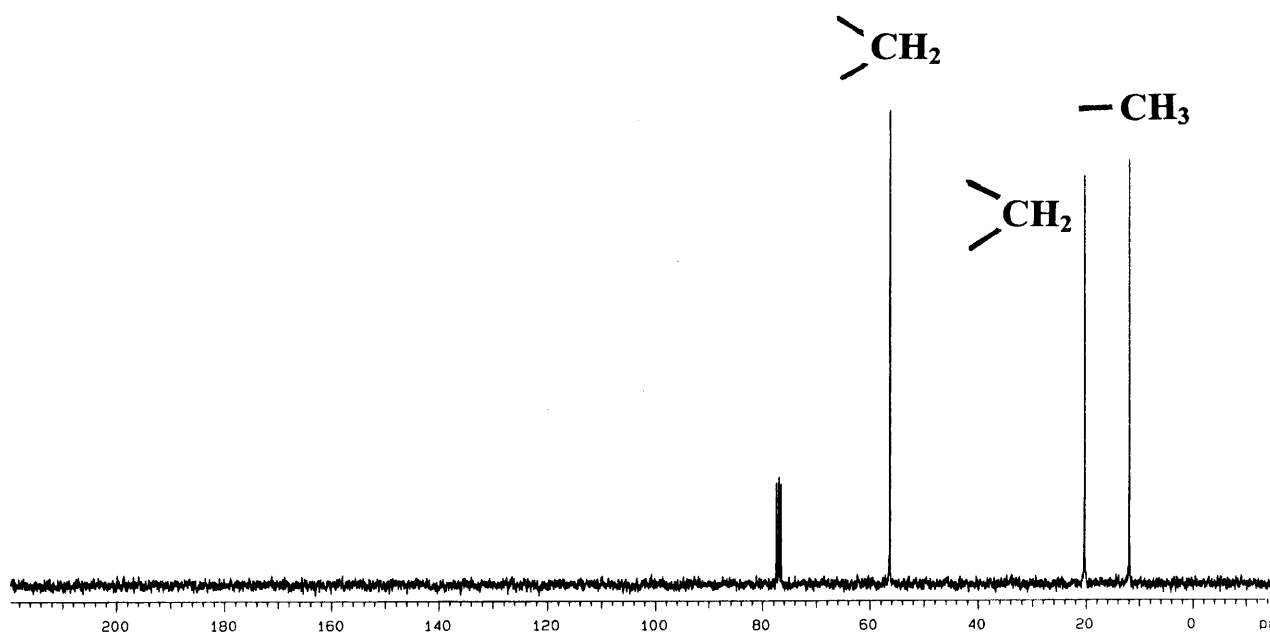


Sample 12.6 Continued

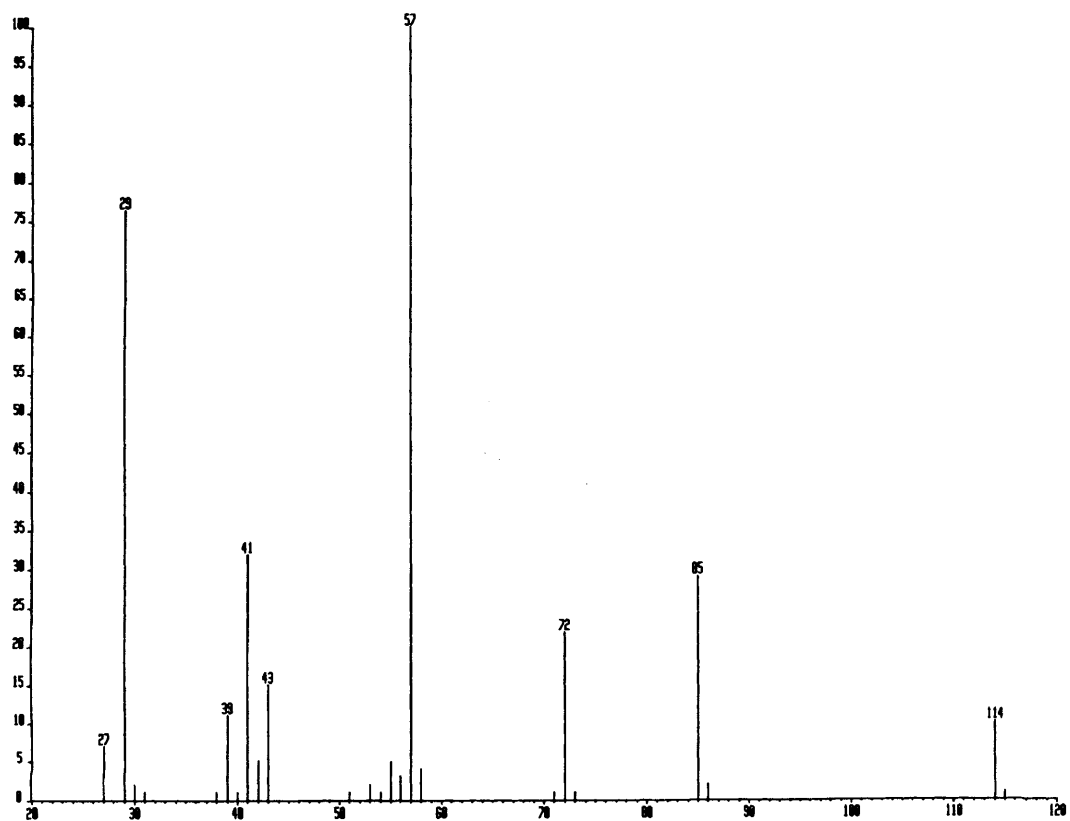
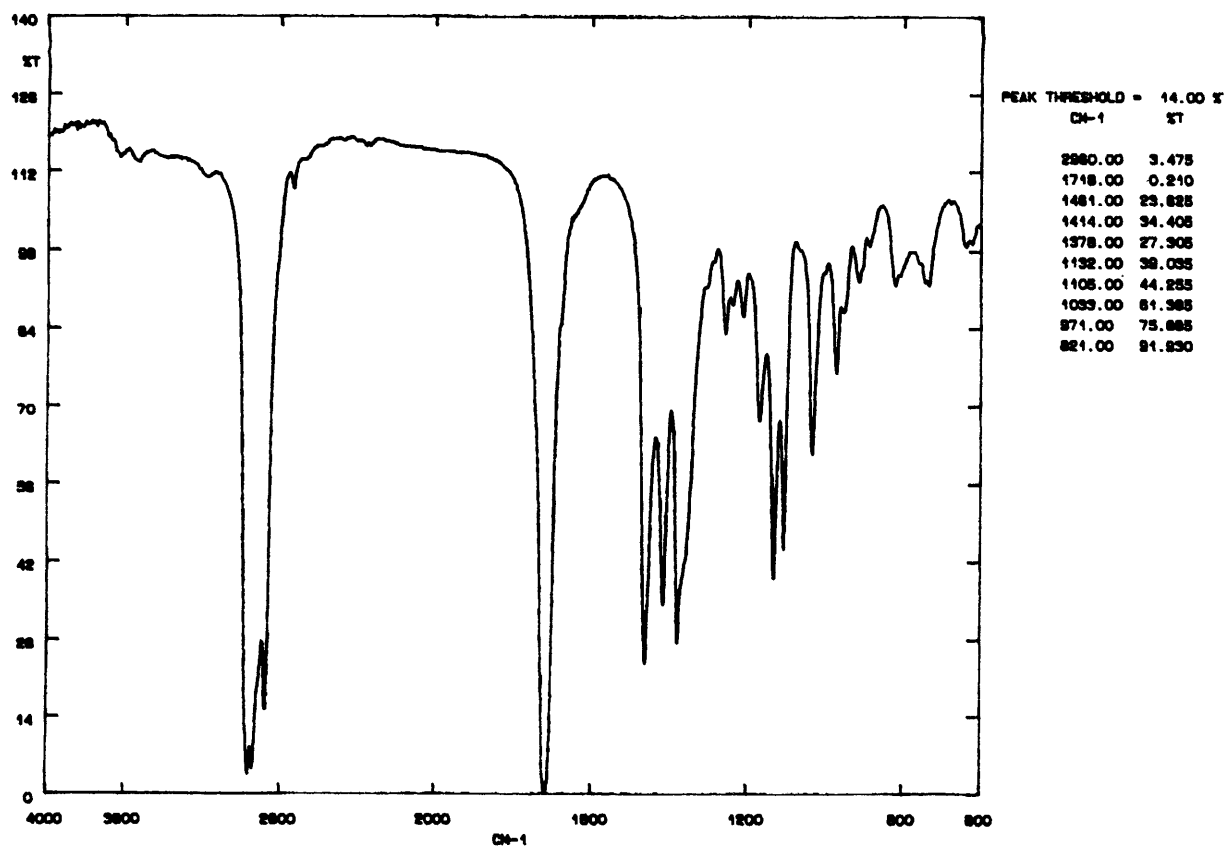


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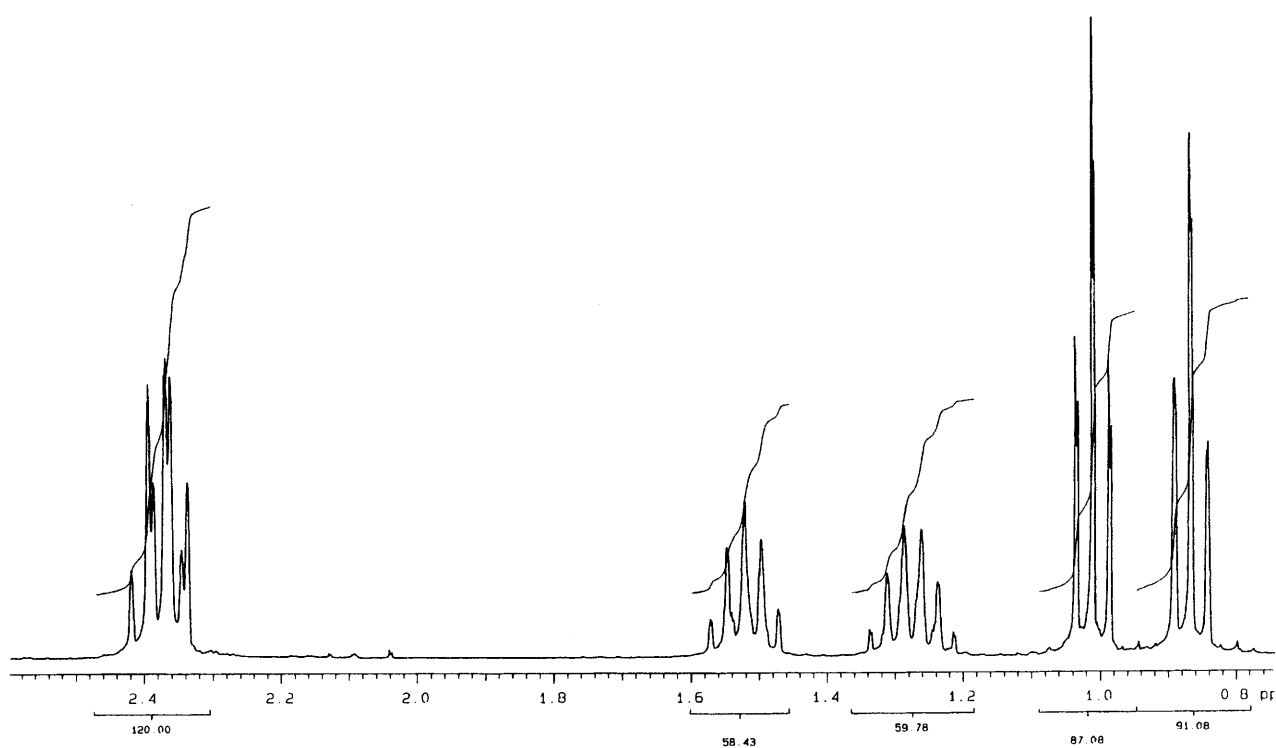
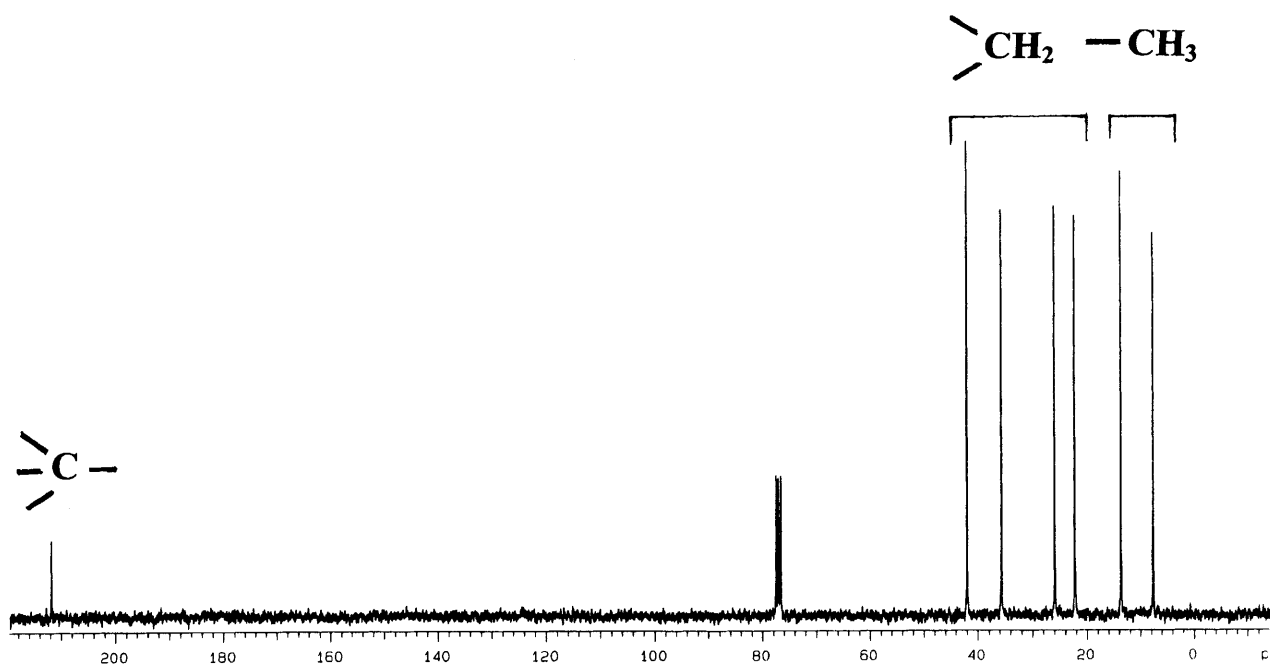




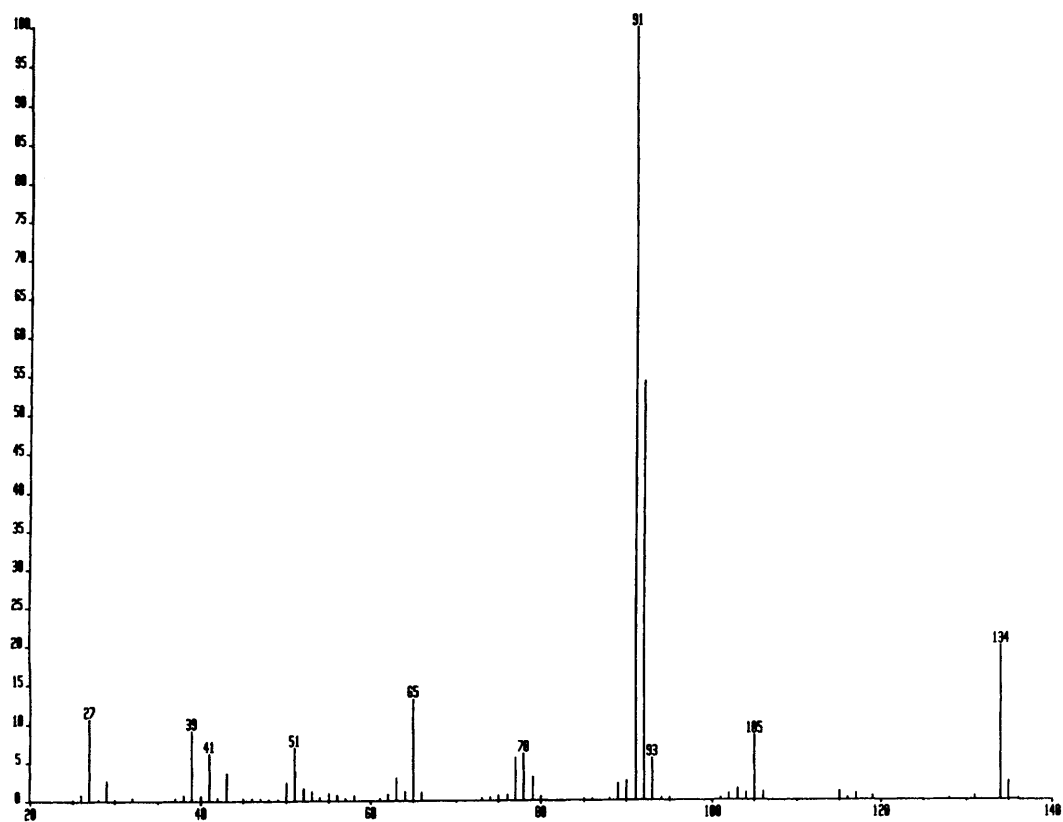
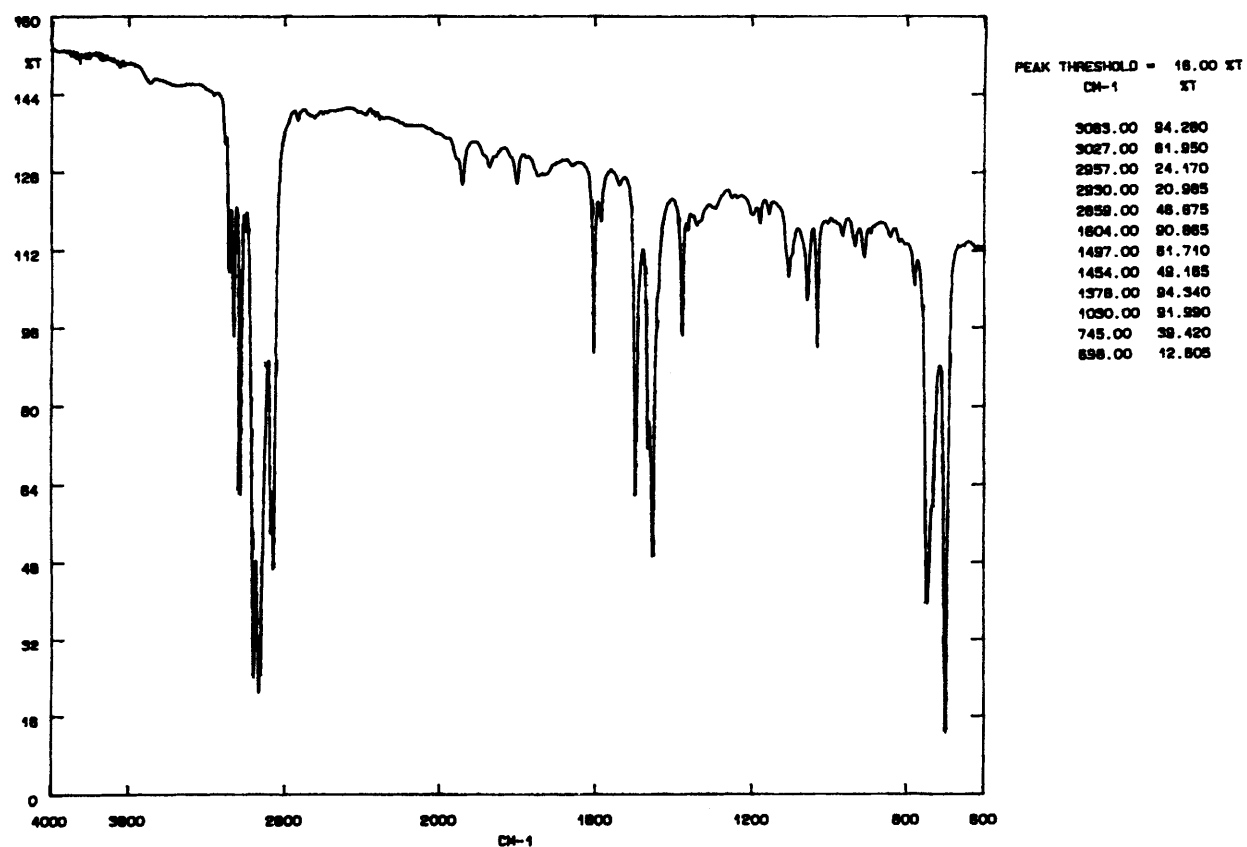
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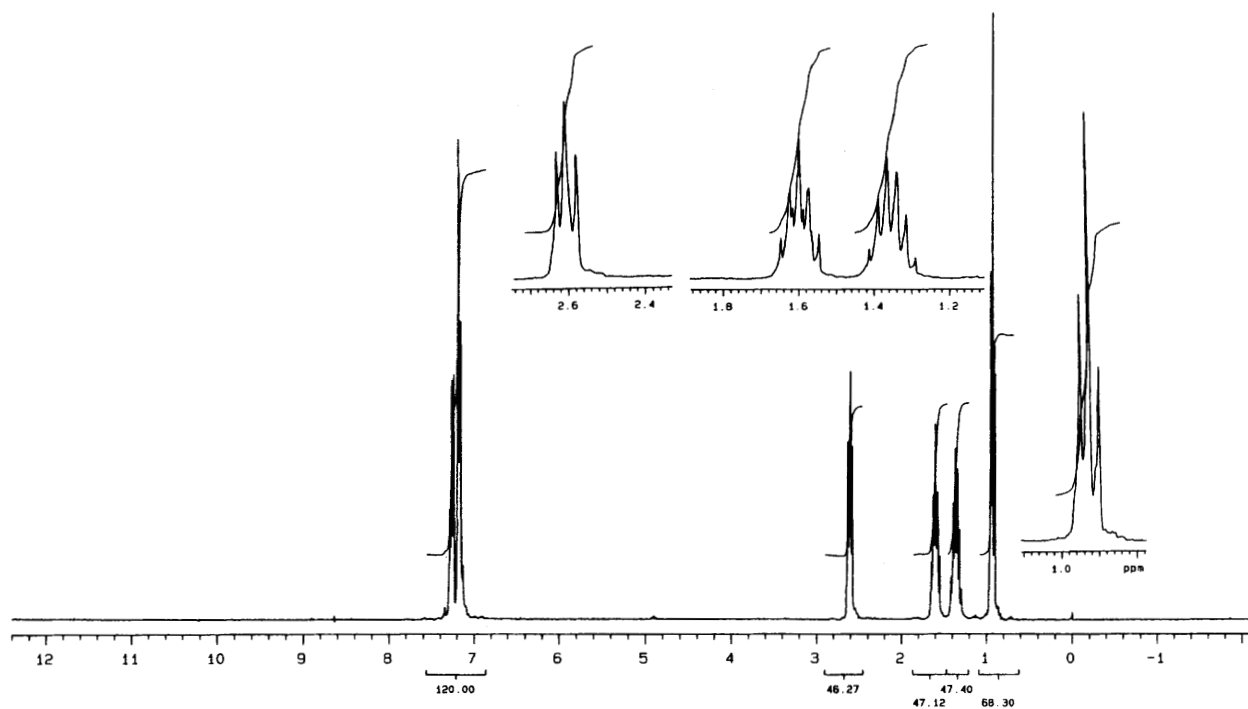
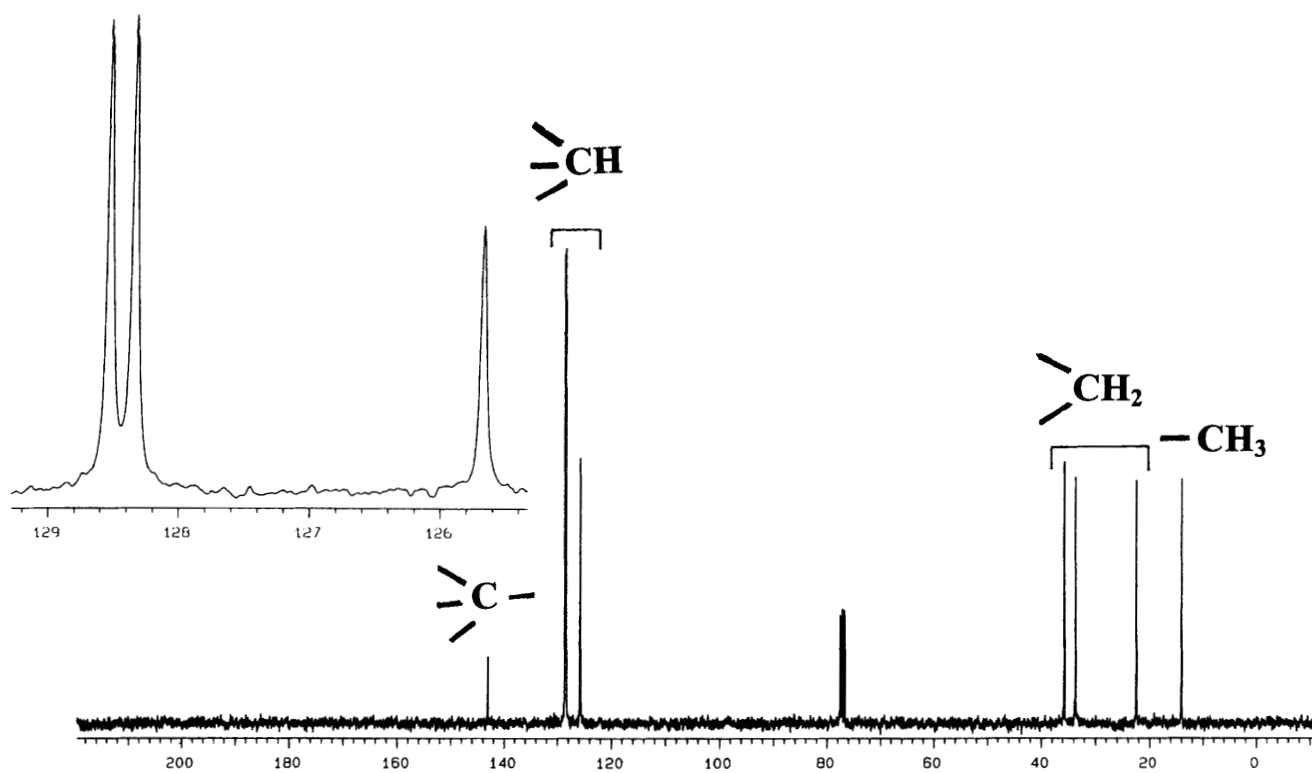
Sample 12.8



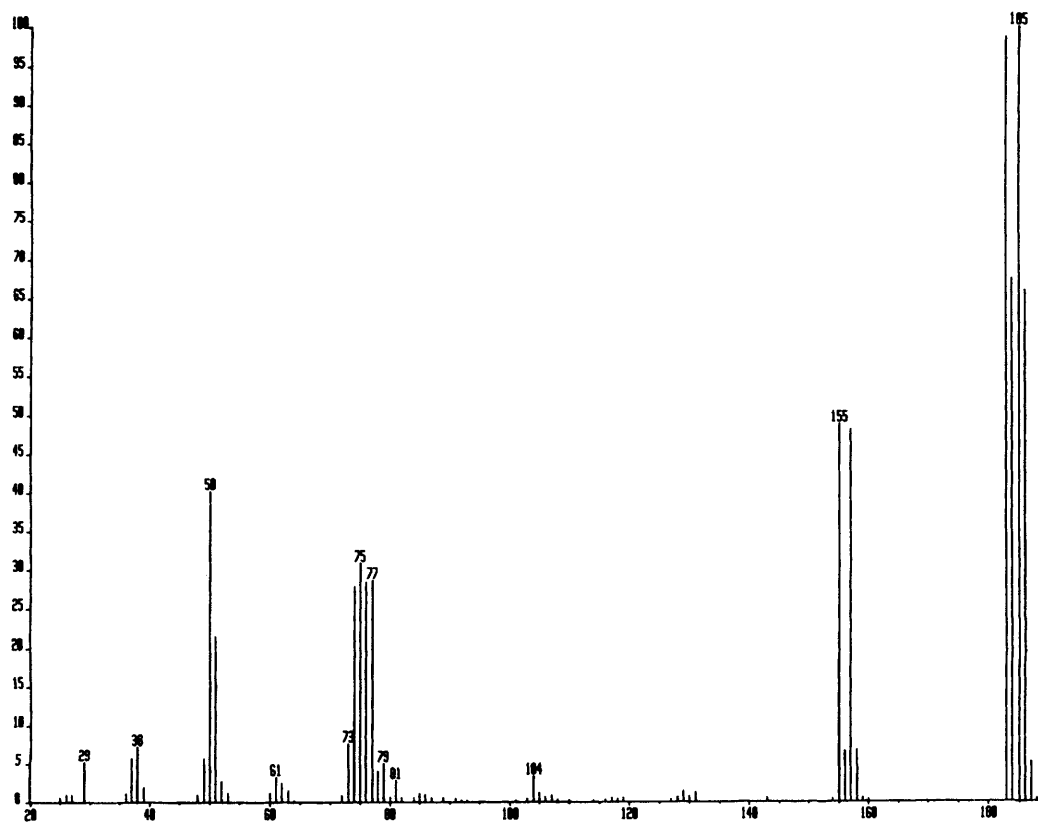
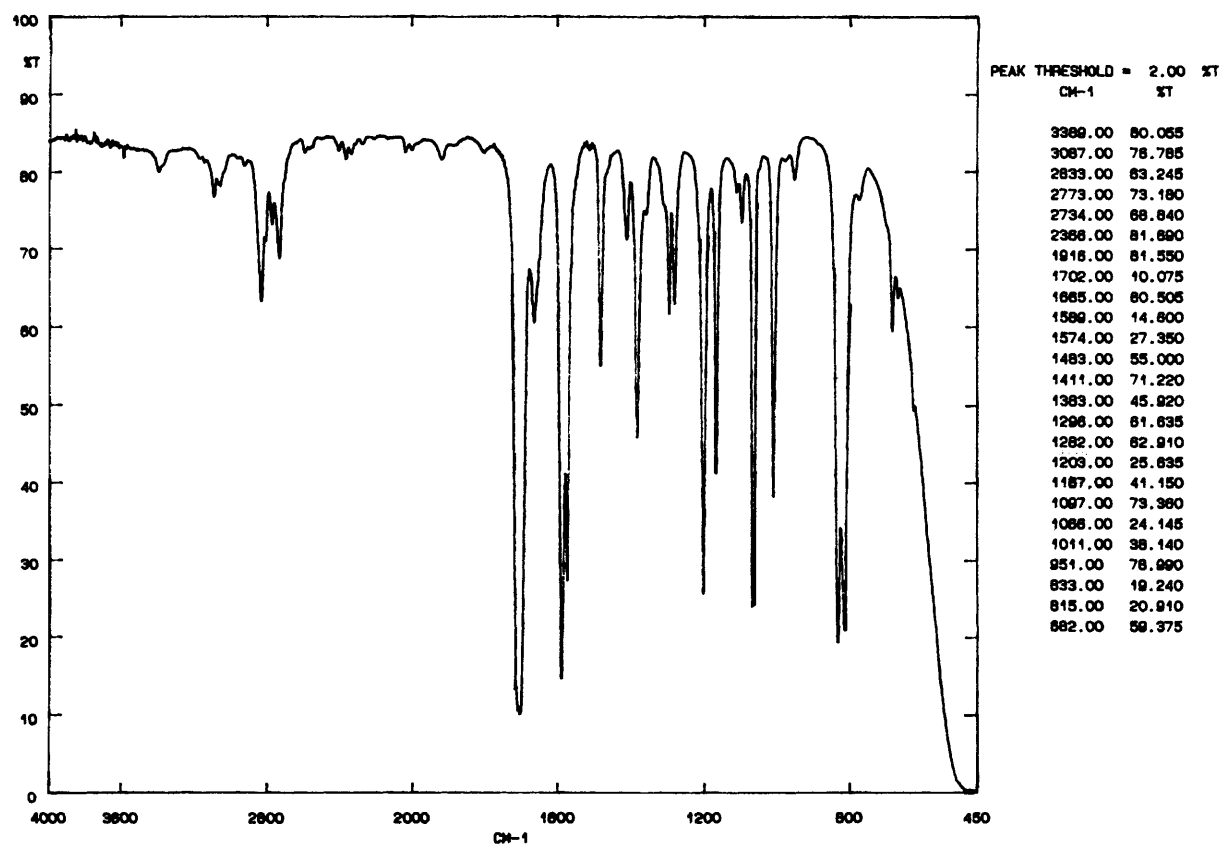
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Sample 12.9



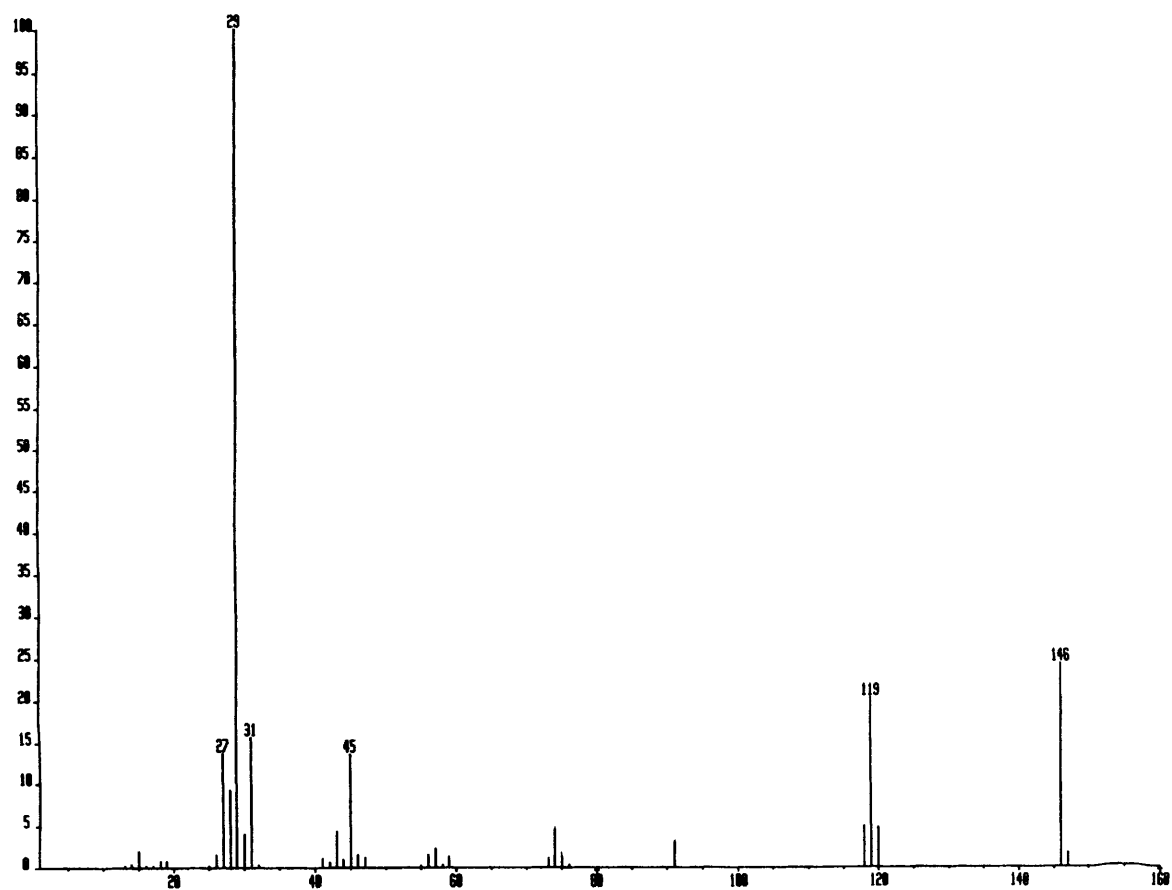
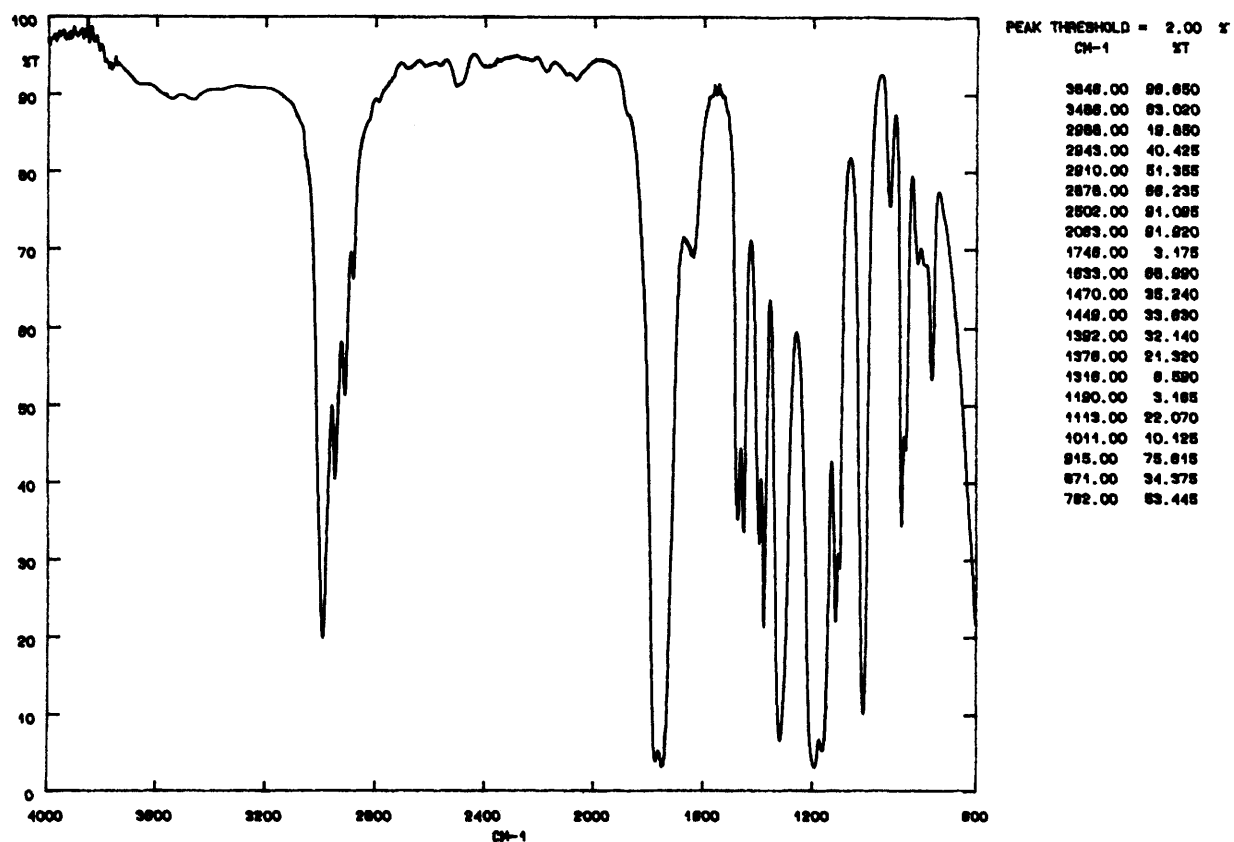
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Sample 12.10

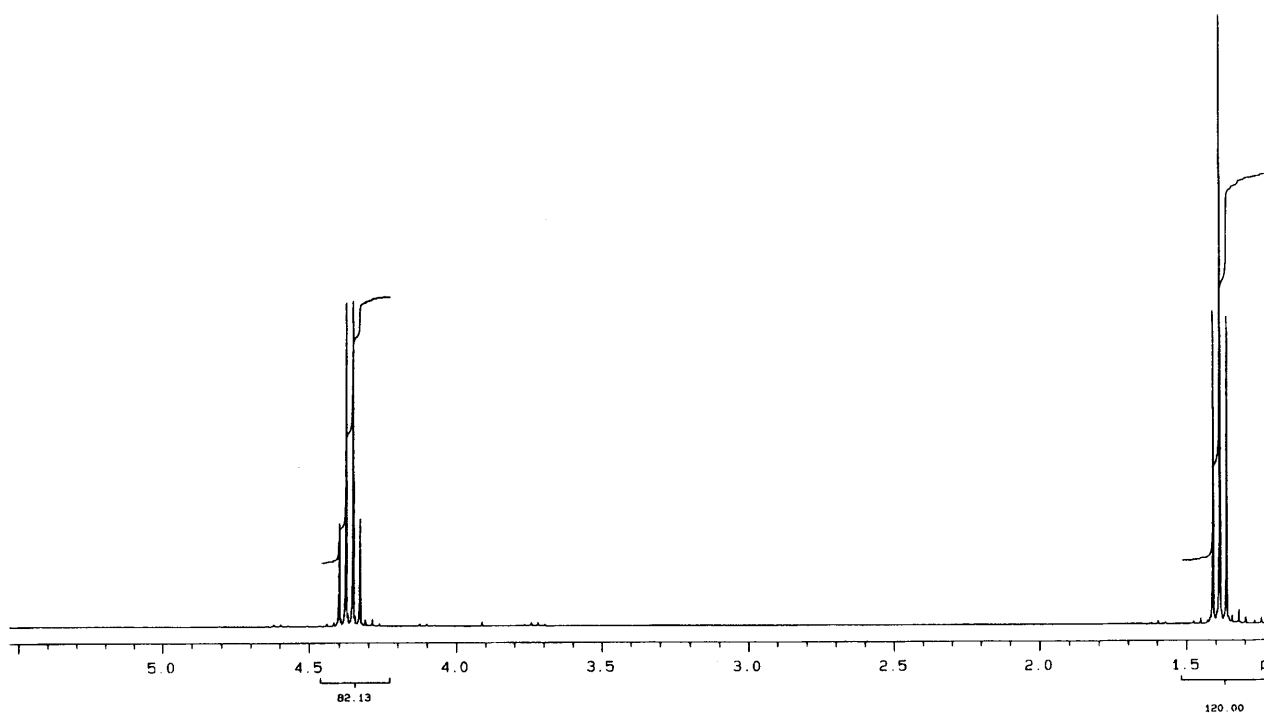
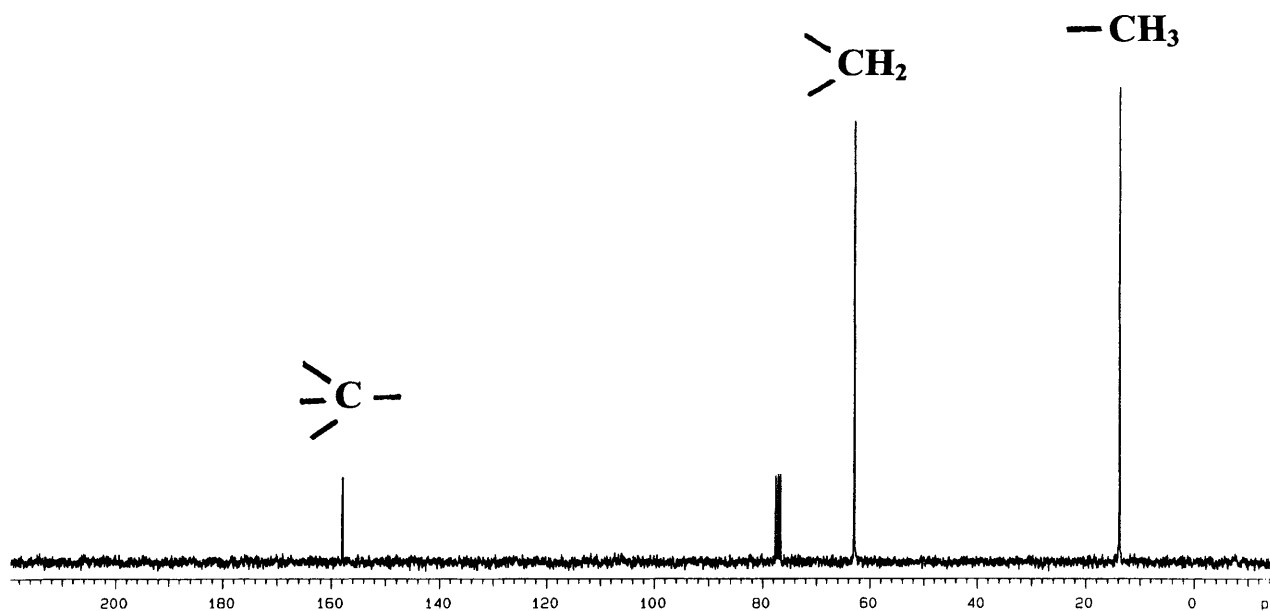


**Sample 12.10 Continued**

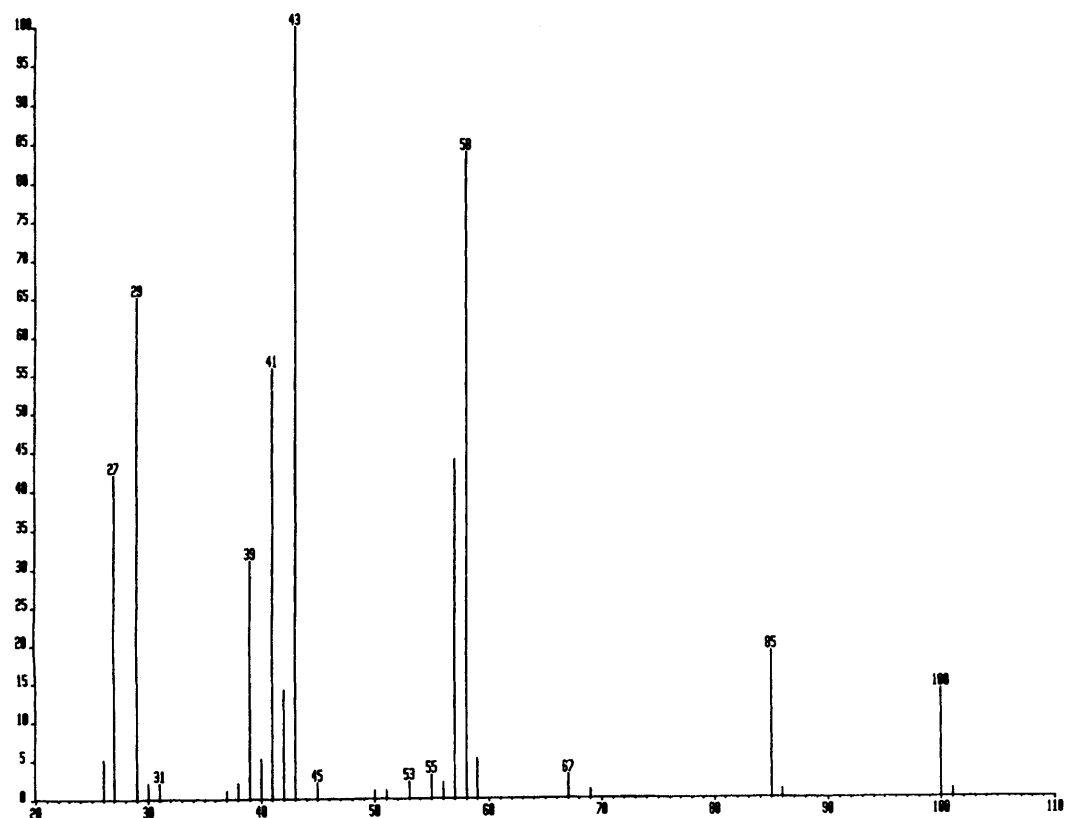
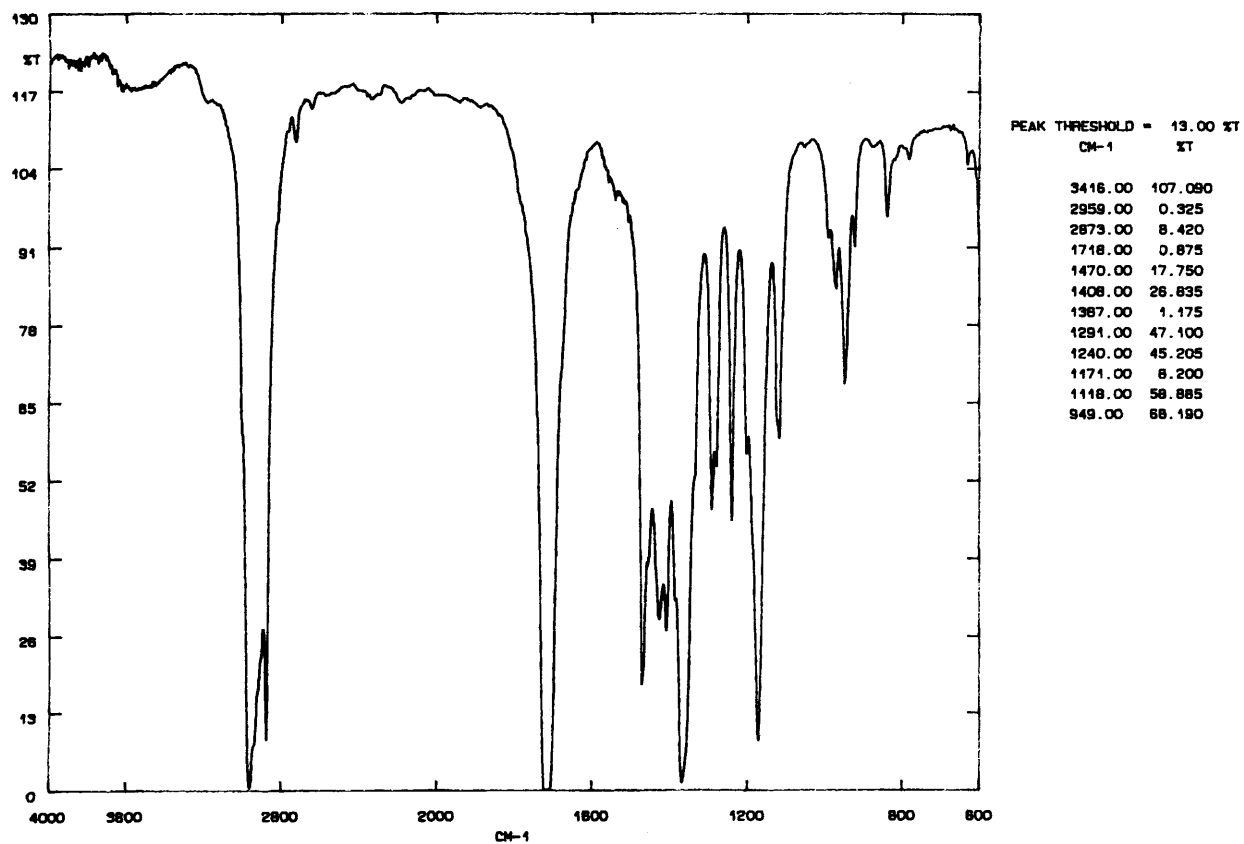


Sample 12.11

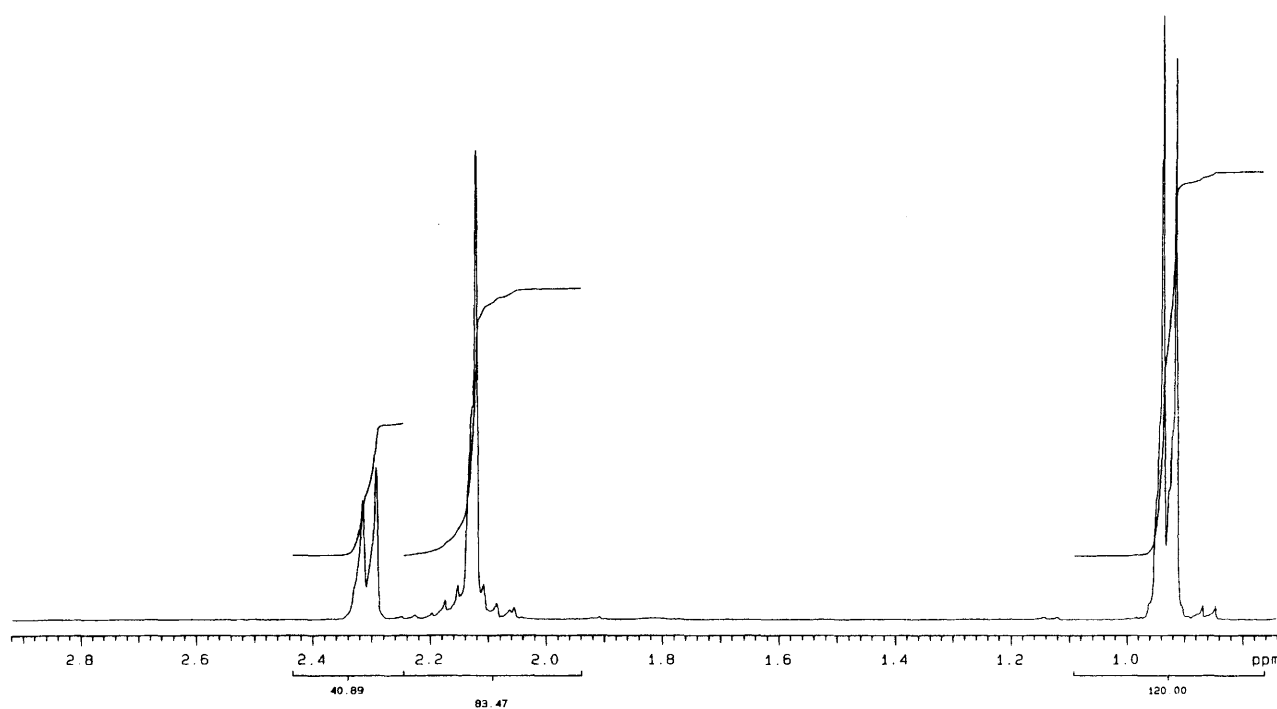
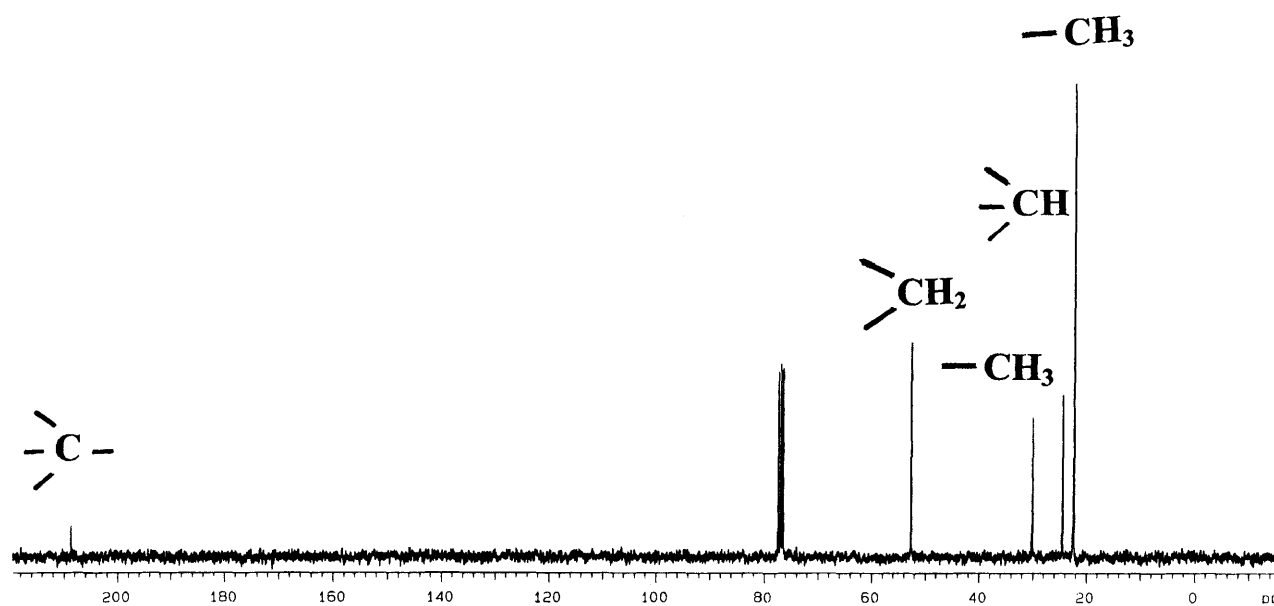




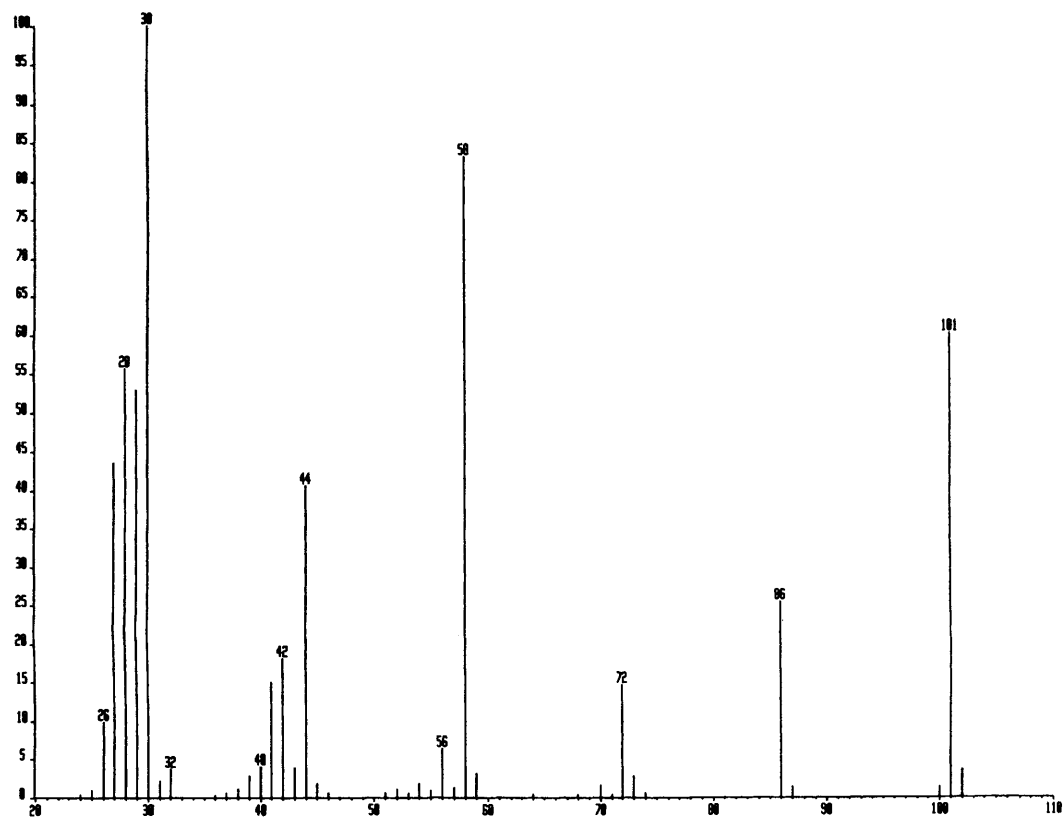
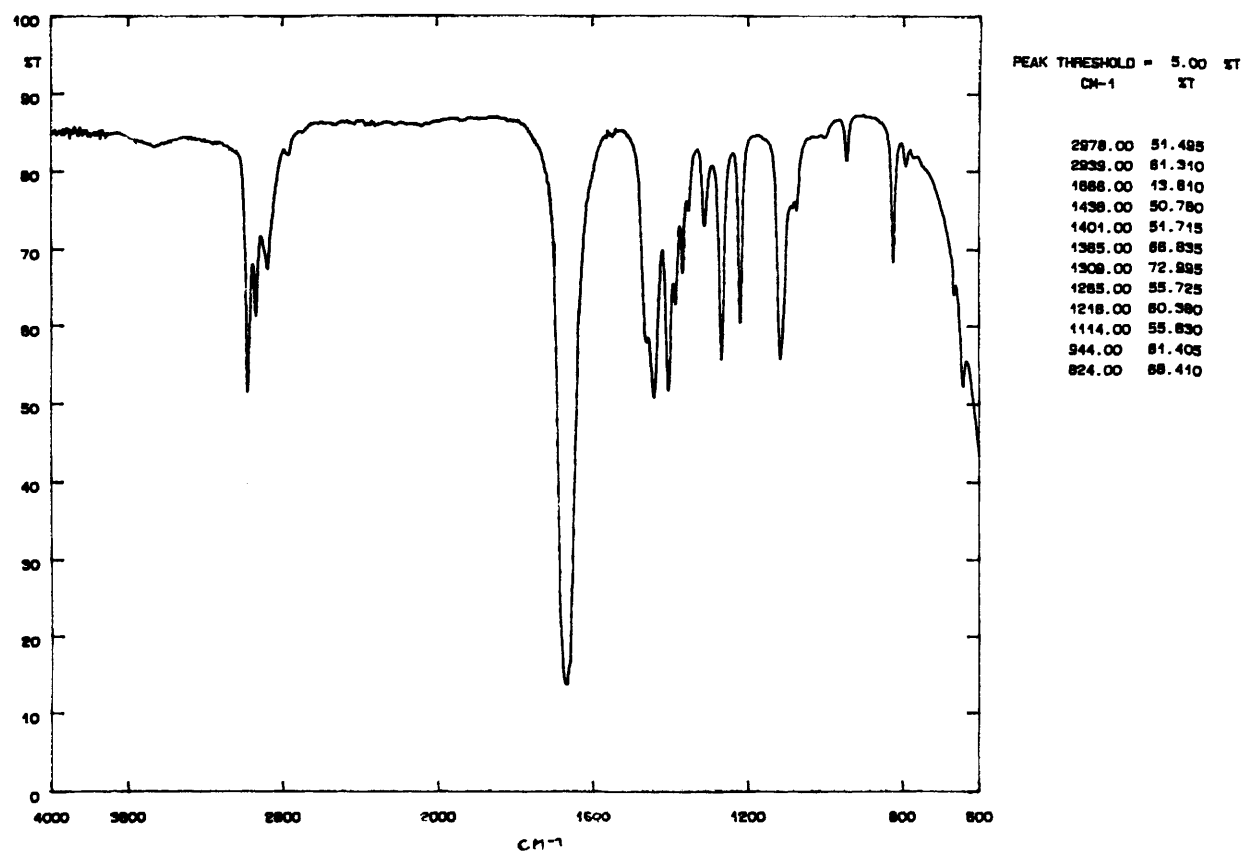
Sample 12.11 Continued



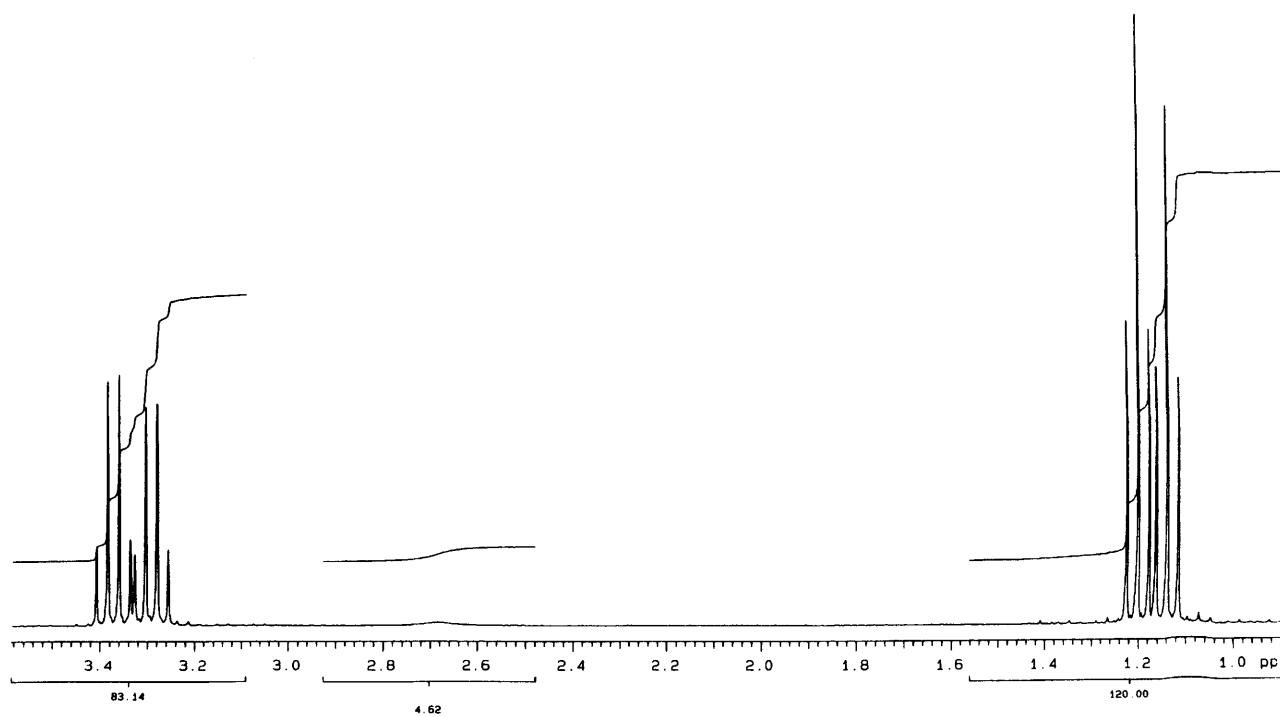
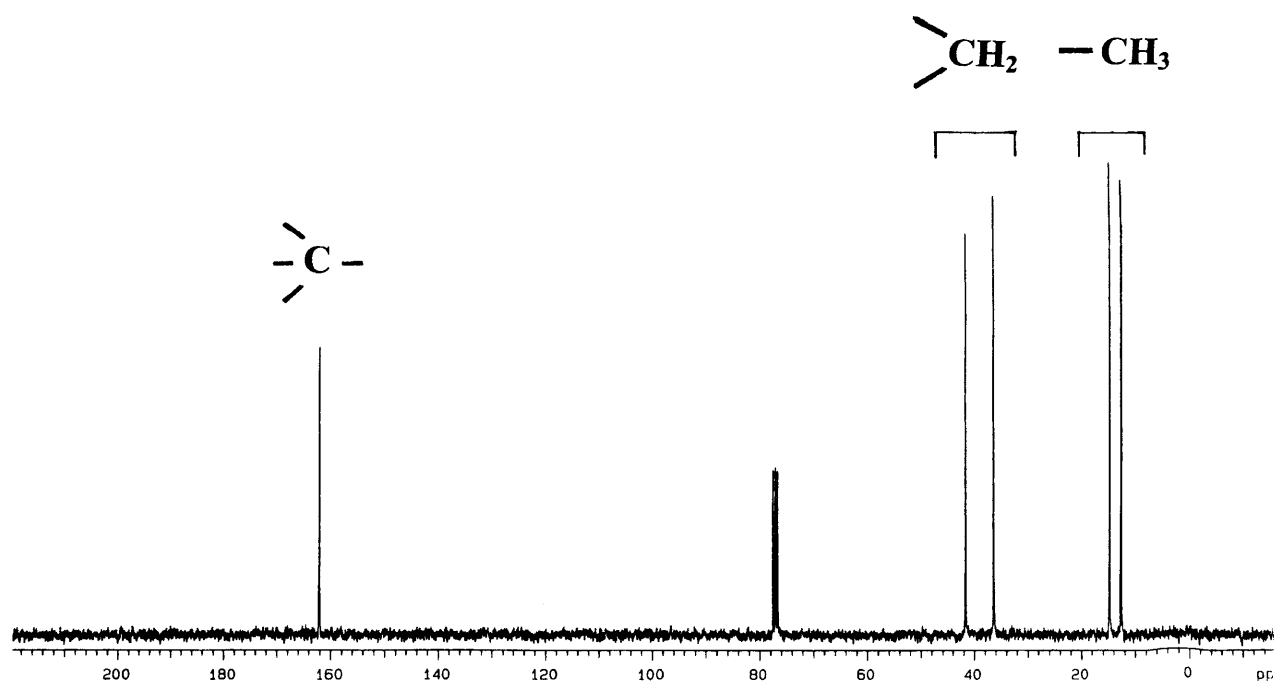
Sample 12.12



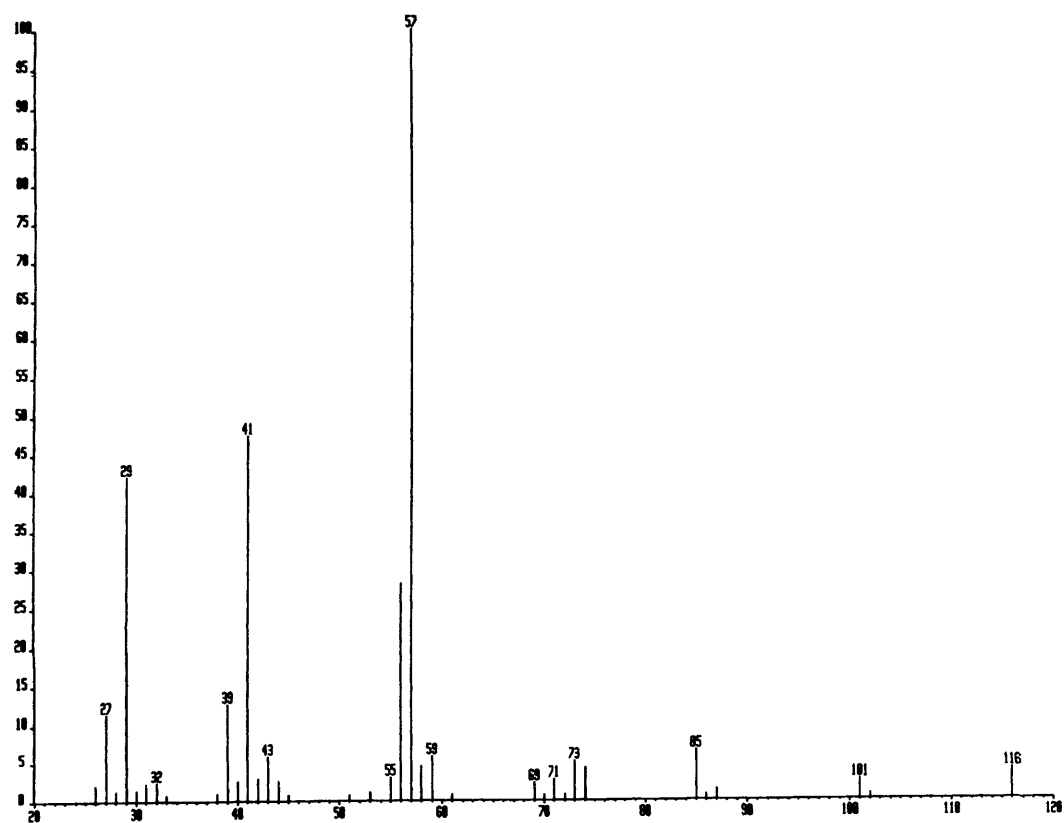
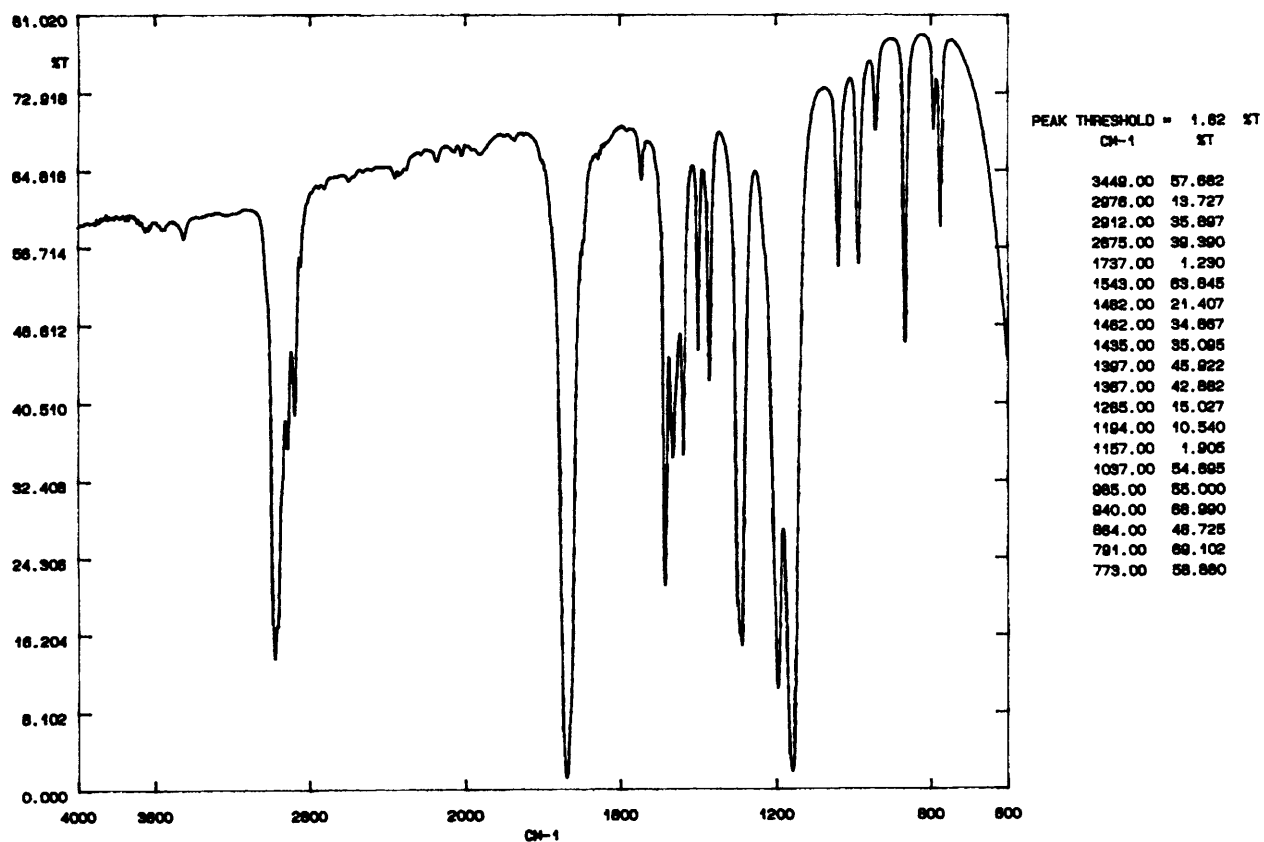
Sample 12.12 Continued



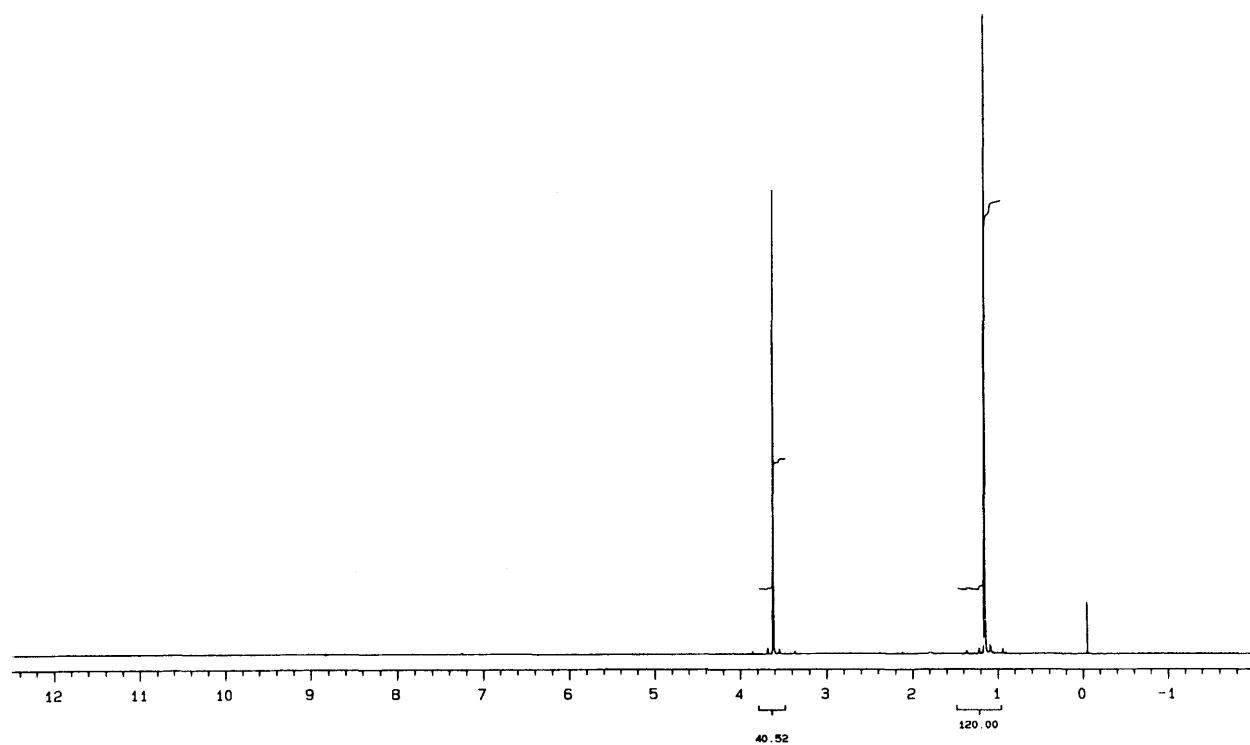
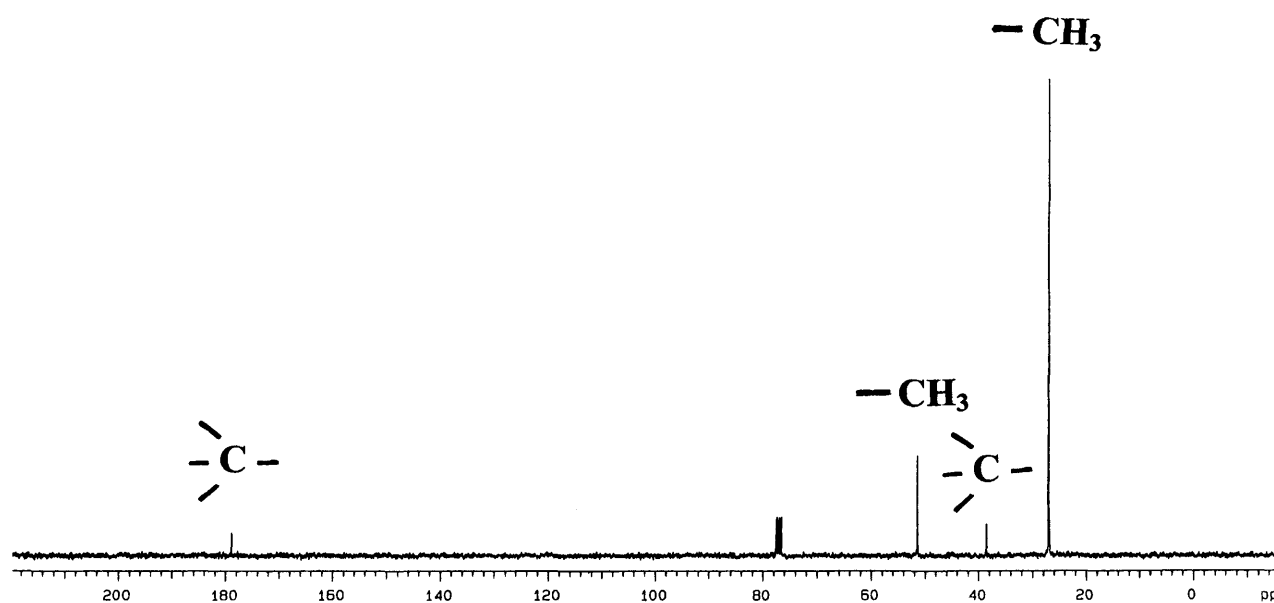
Sample 12.13



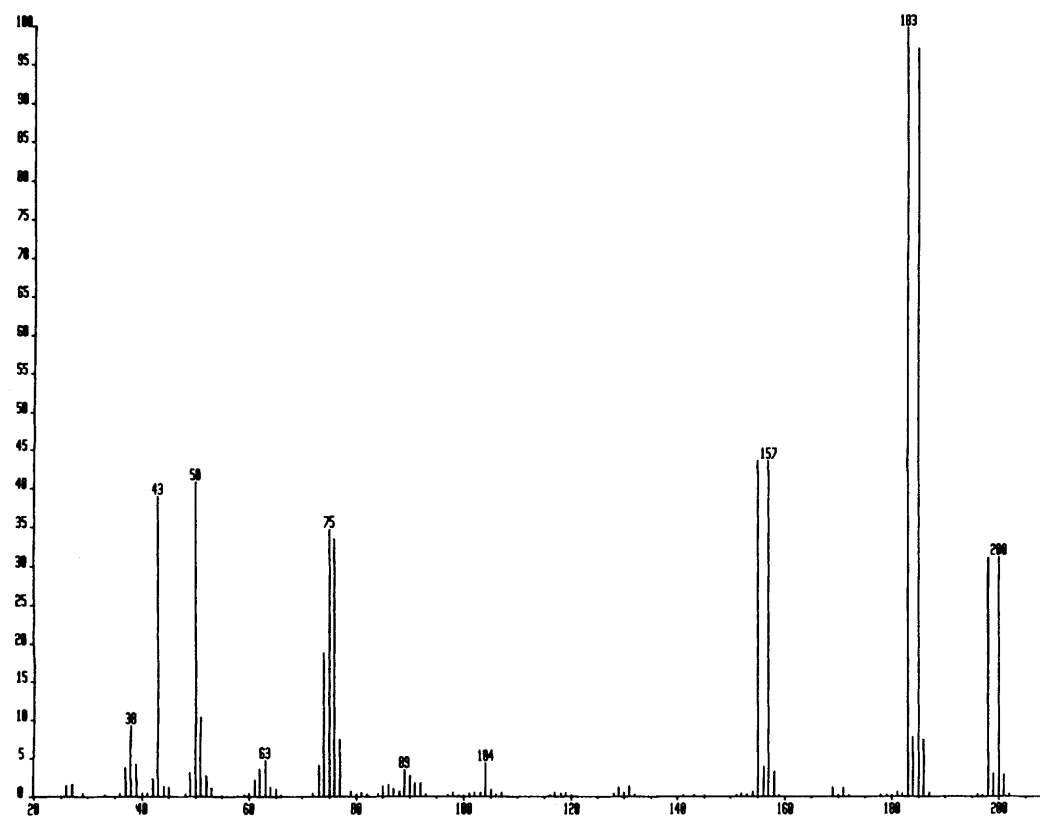
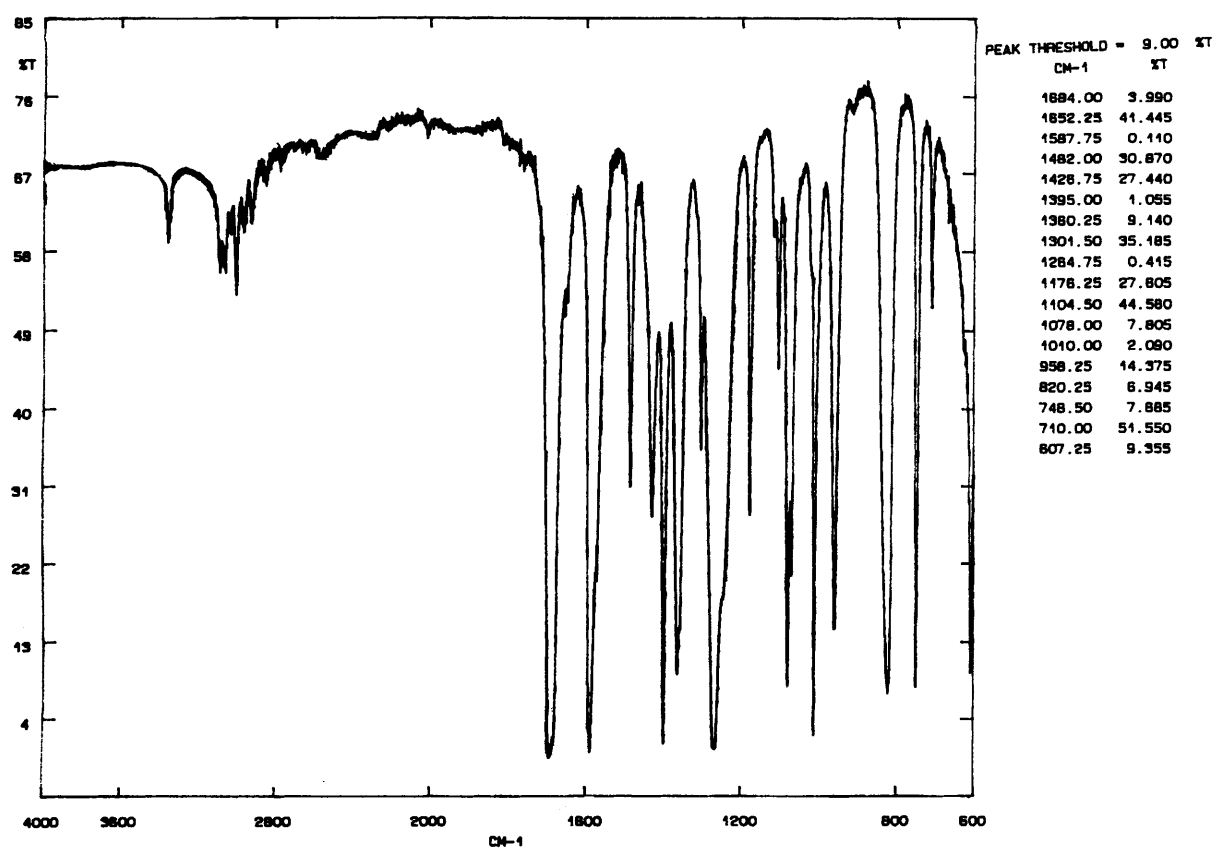
Sample 12.13 Continued



Sample 12.14

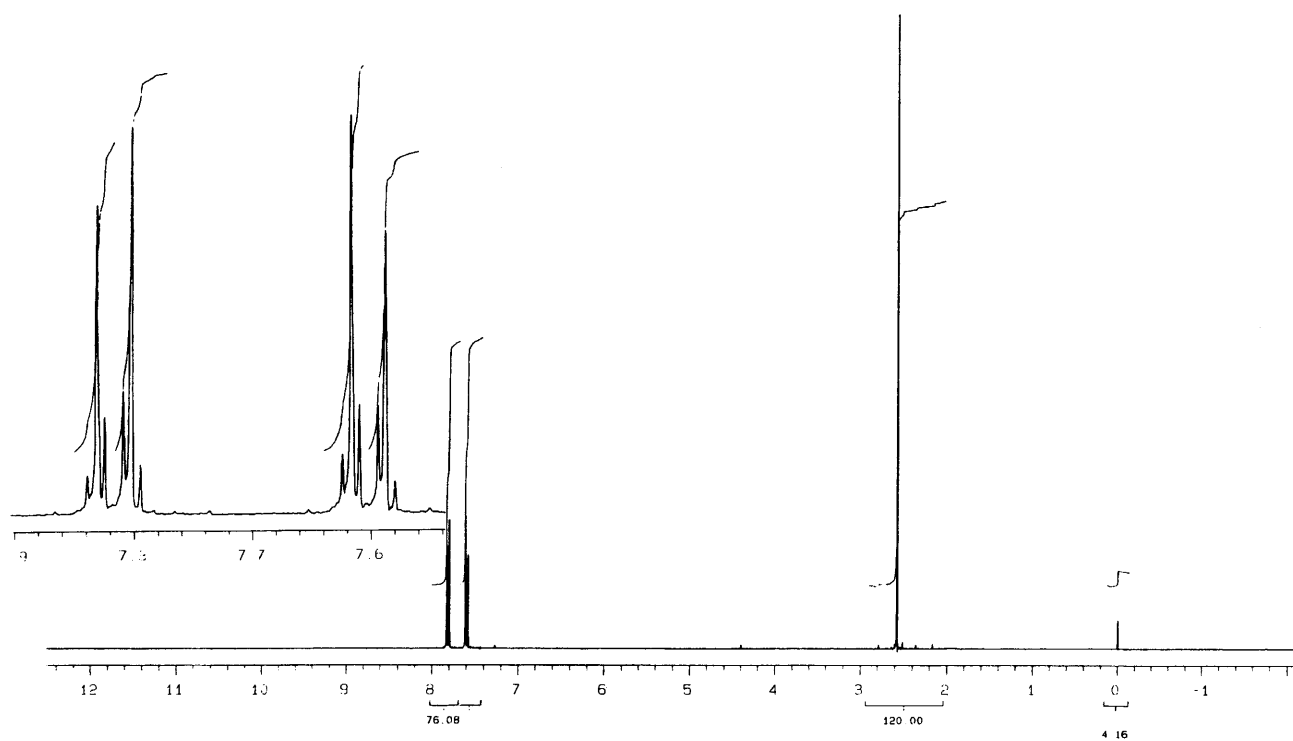
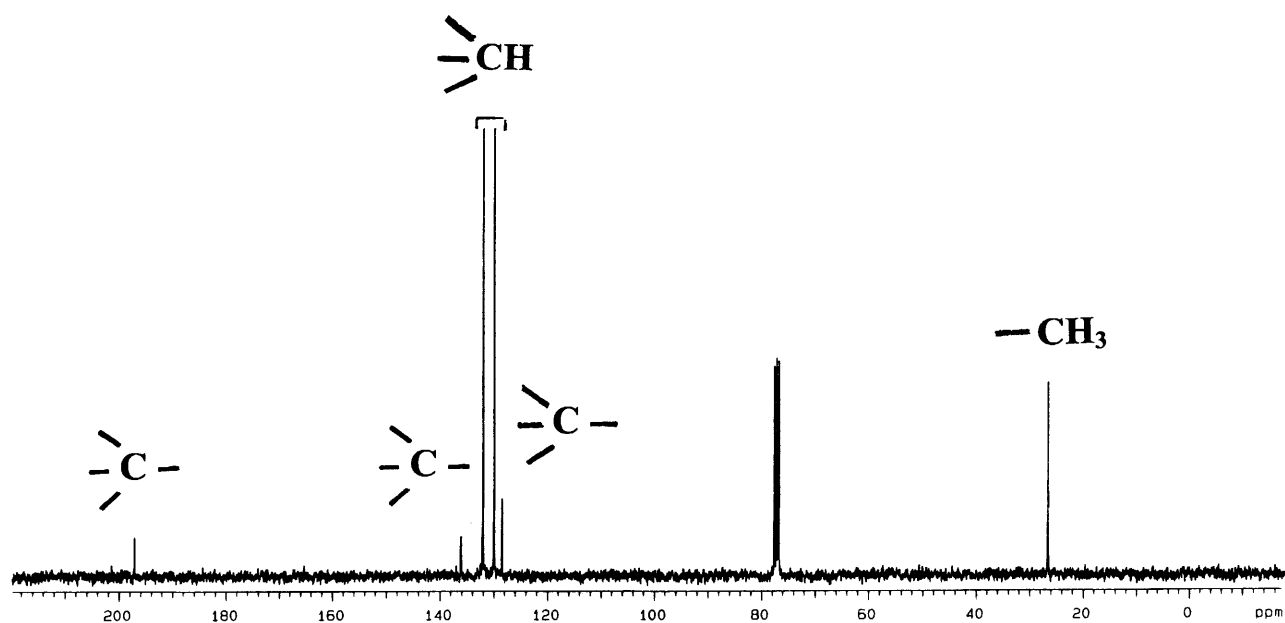


Sample 12.14 Continued

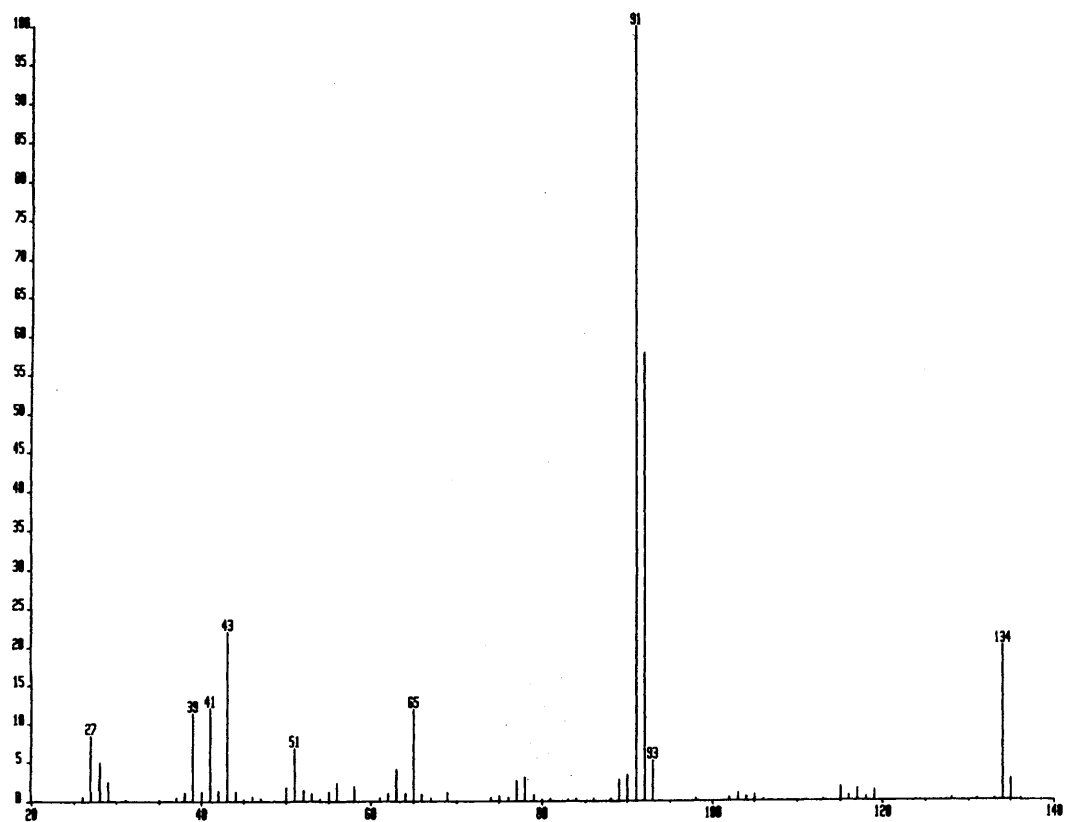
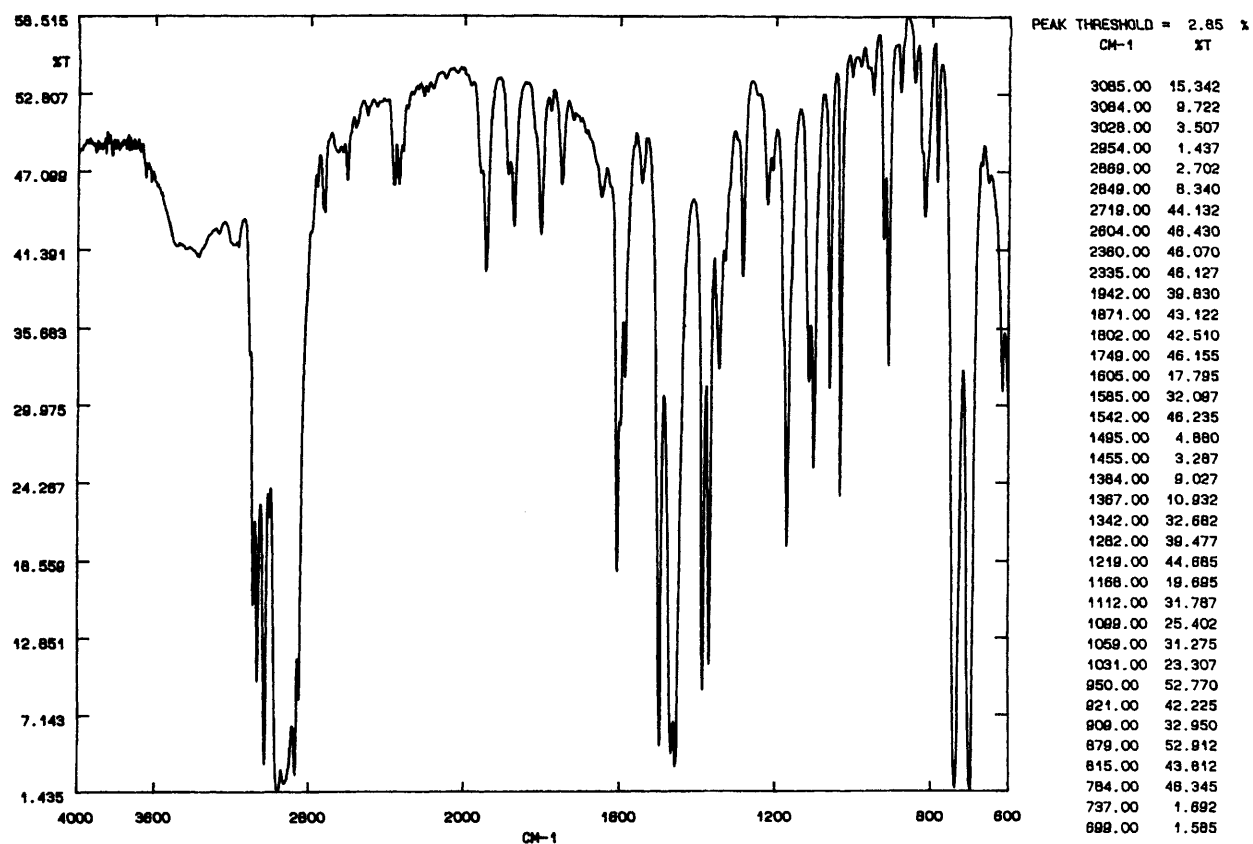


Sample 12.15

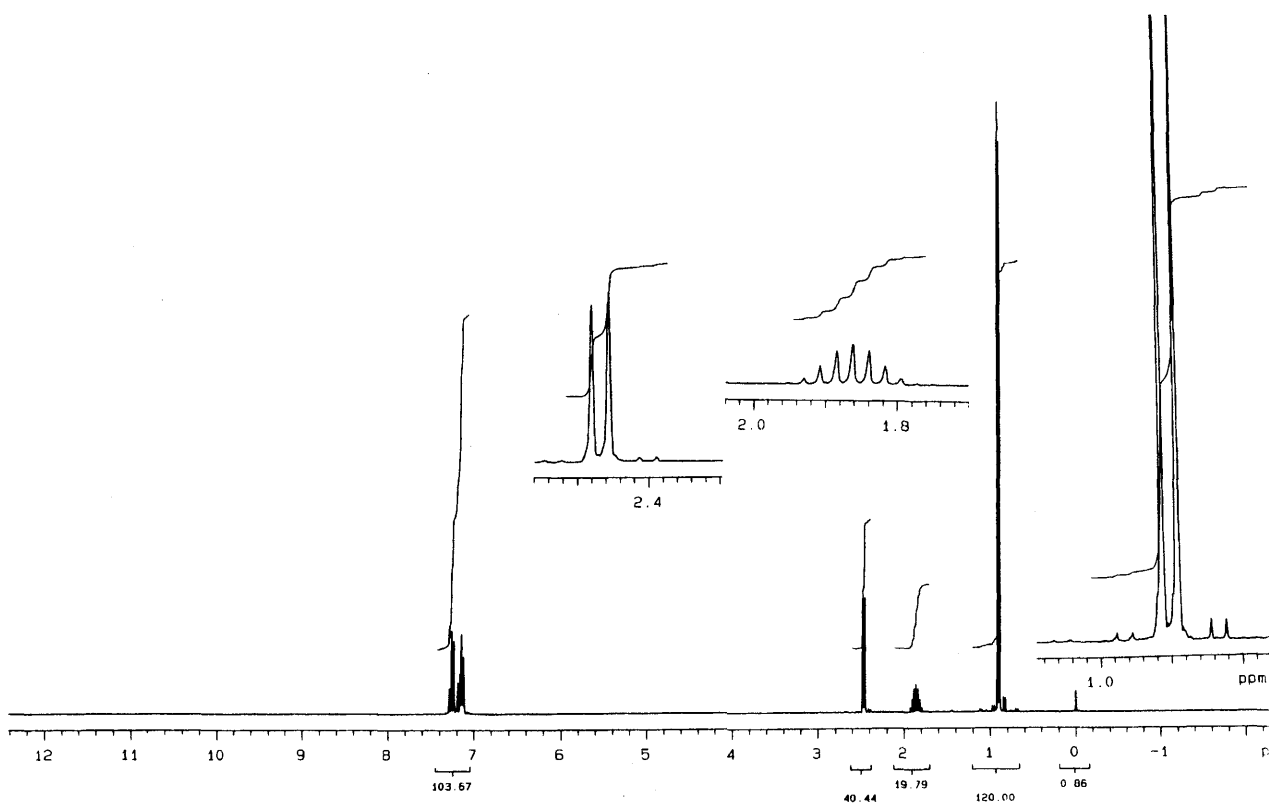
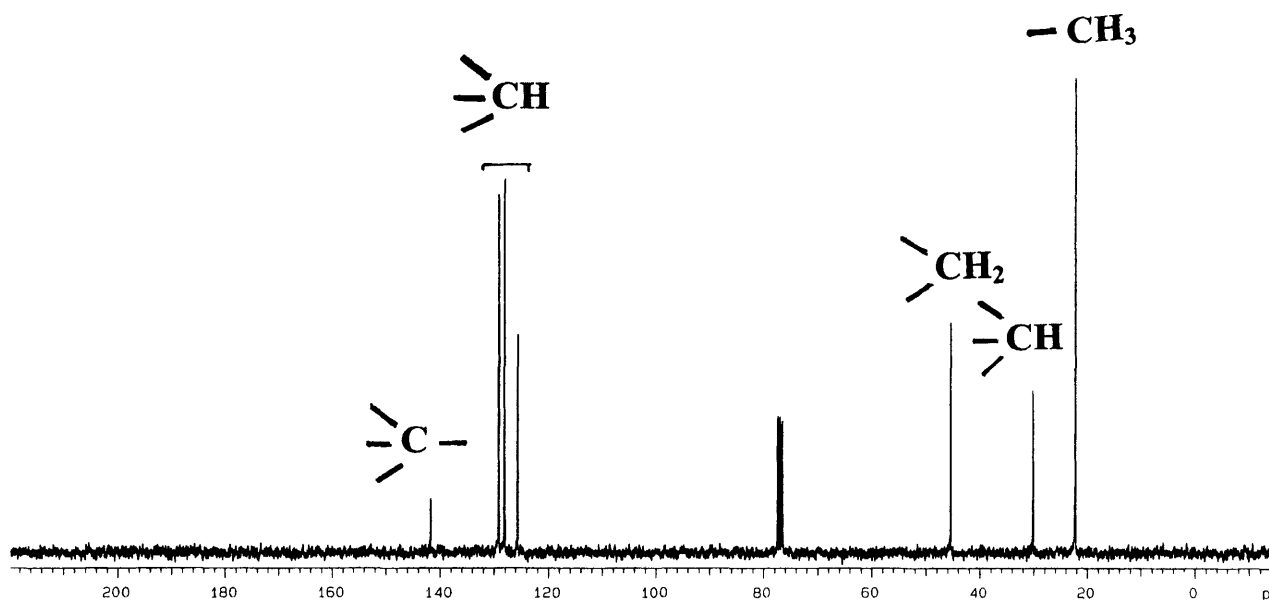




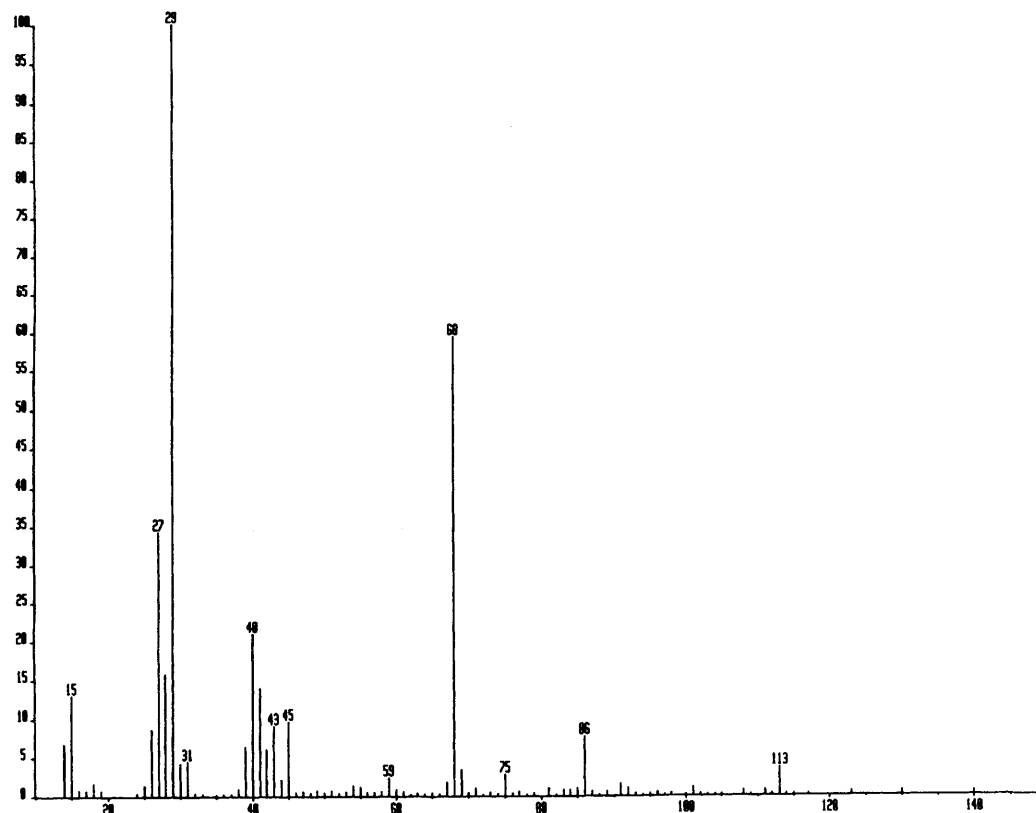
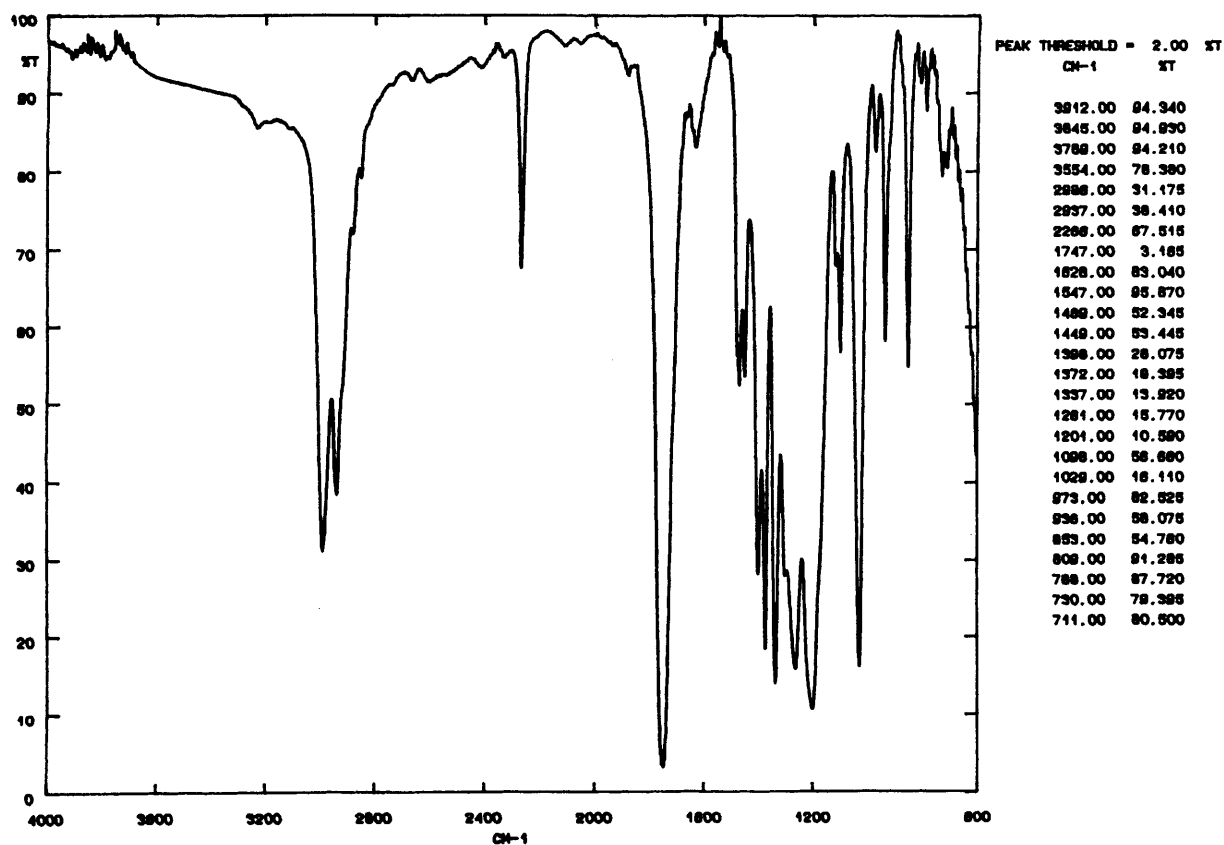
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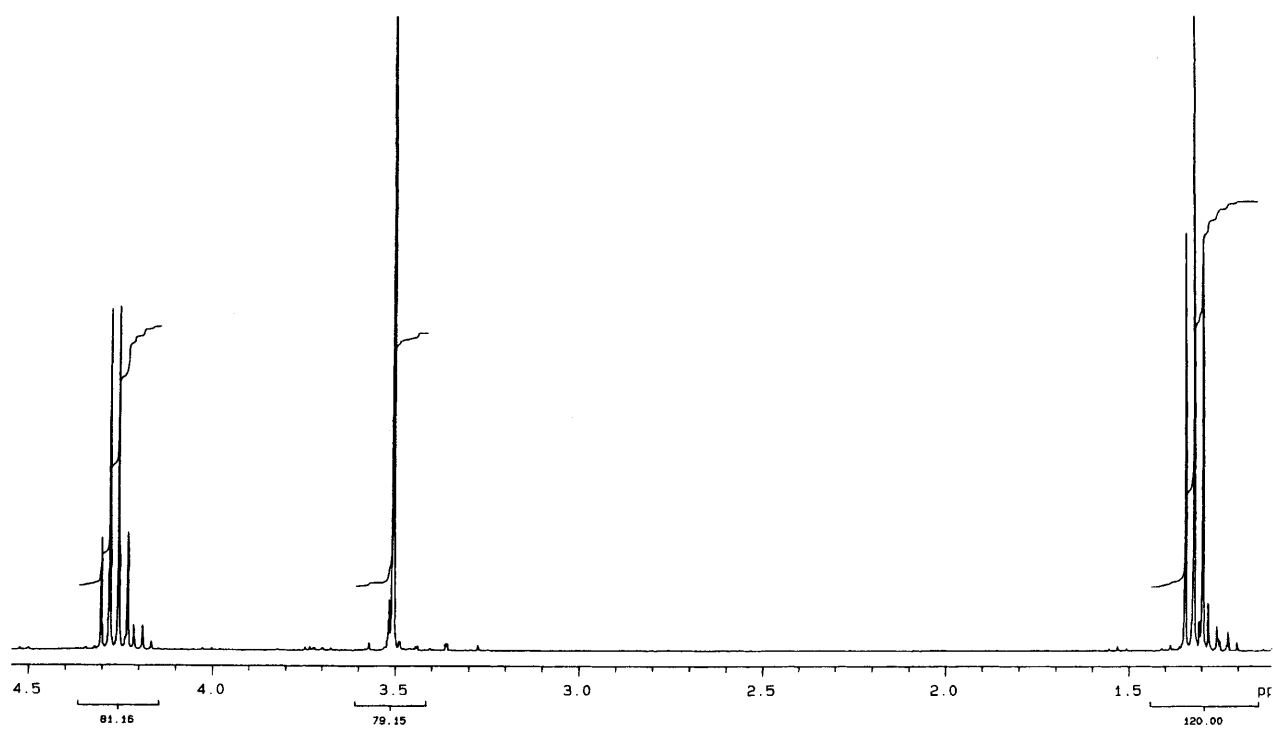
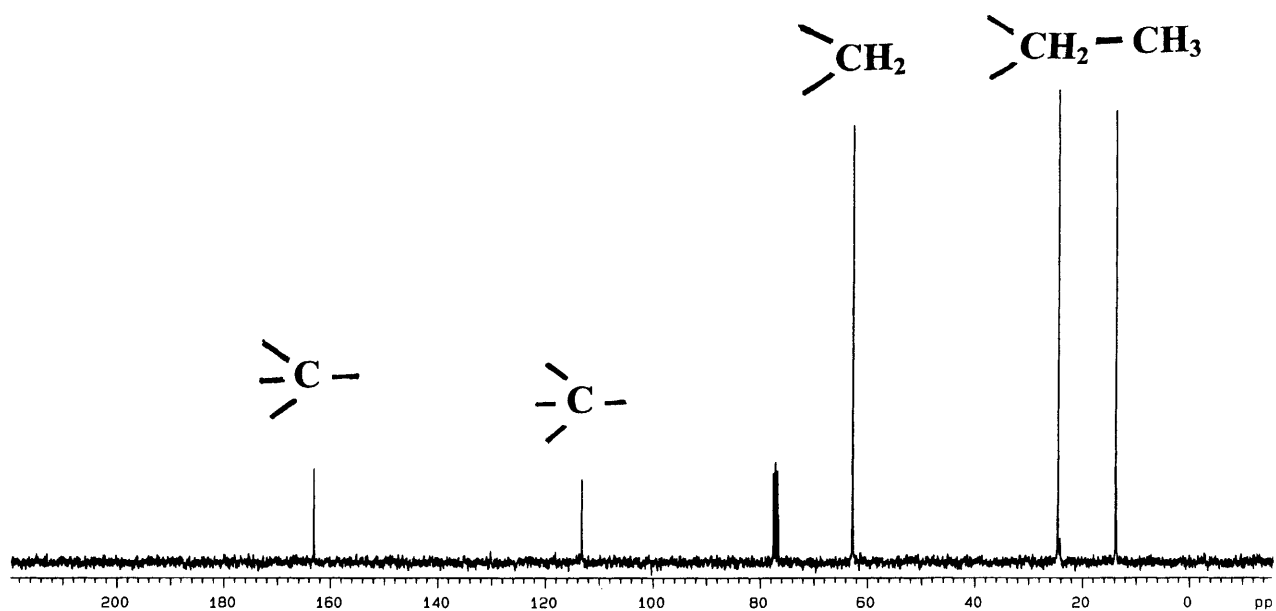
Sample 12.16



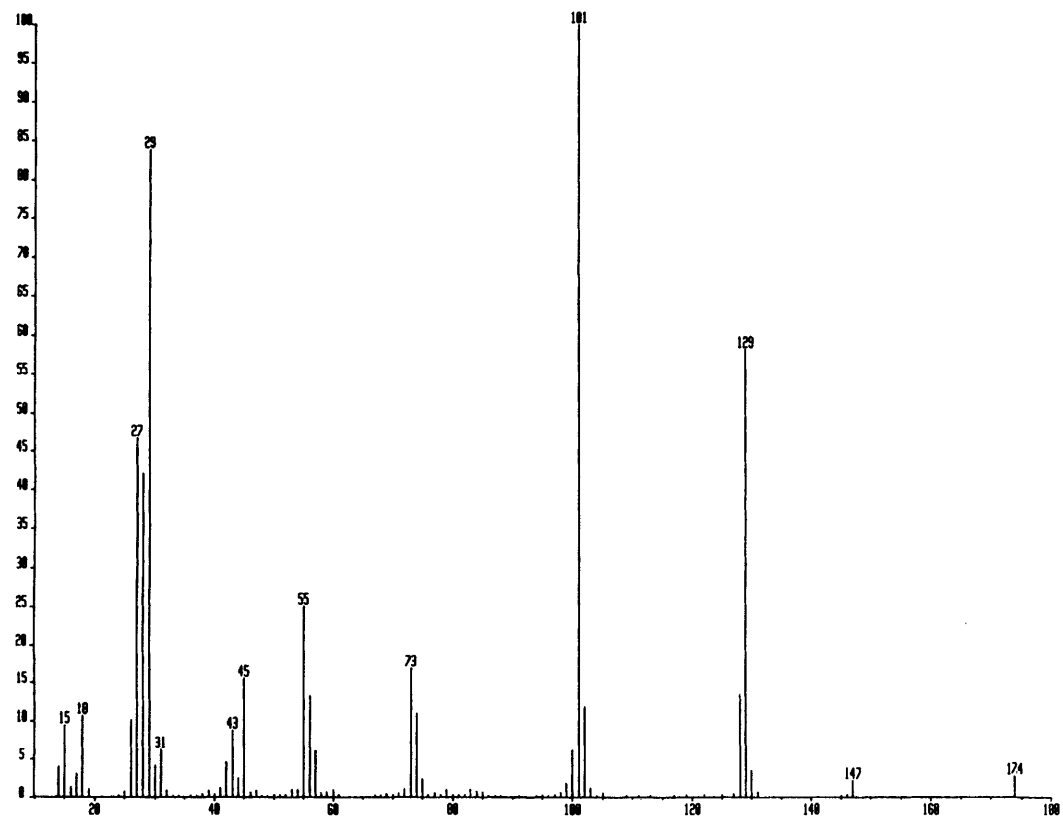
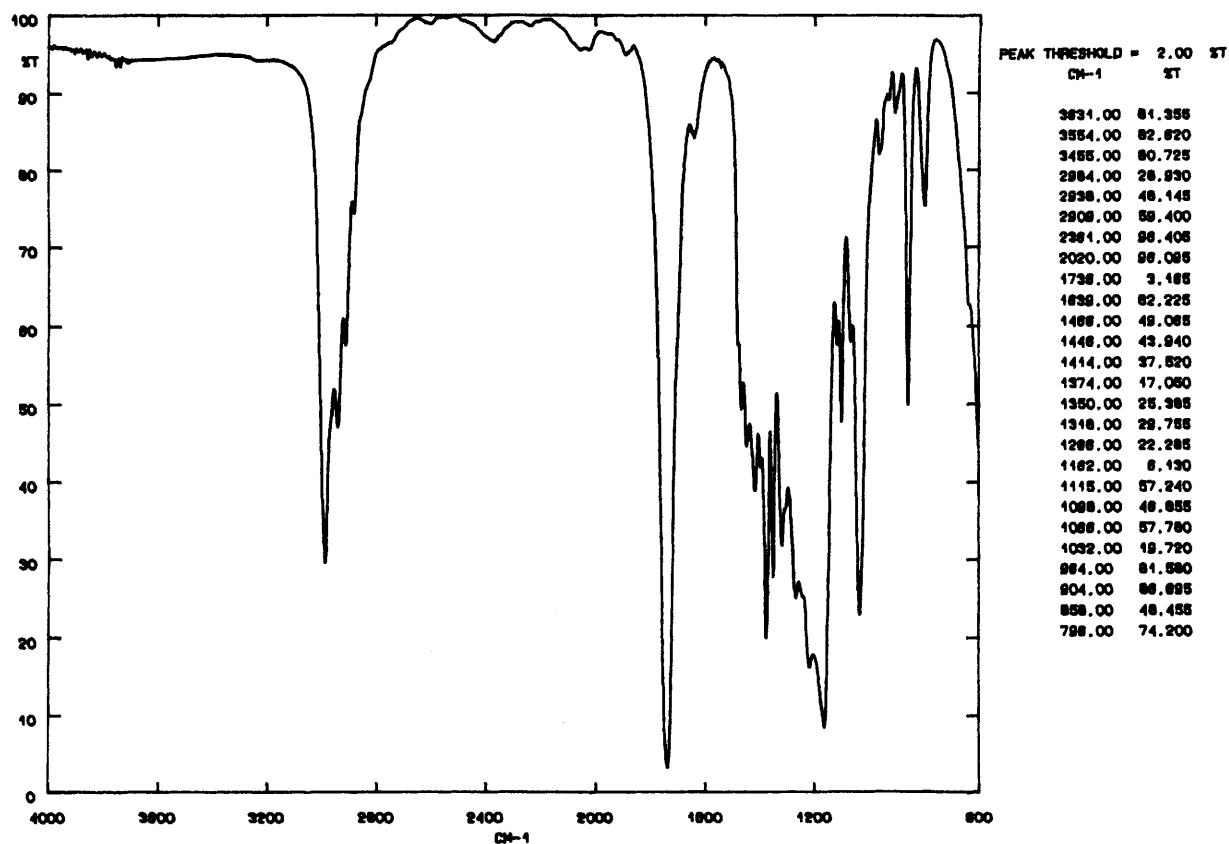
Sample 12.16 Continued



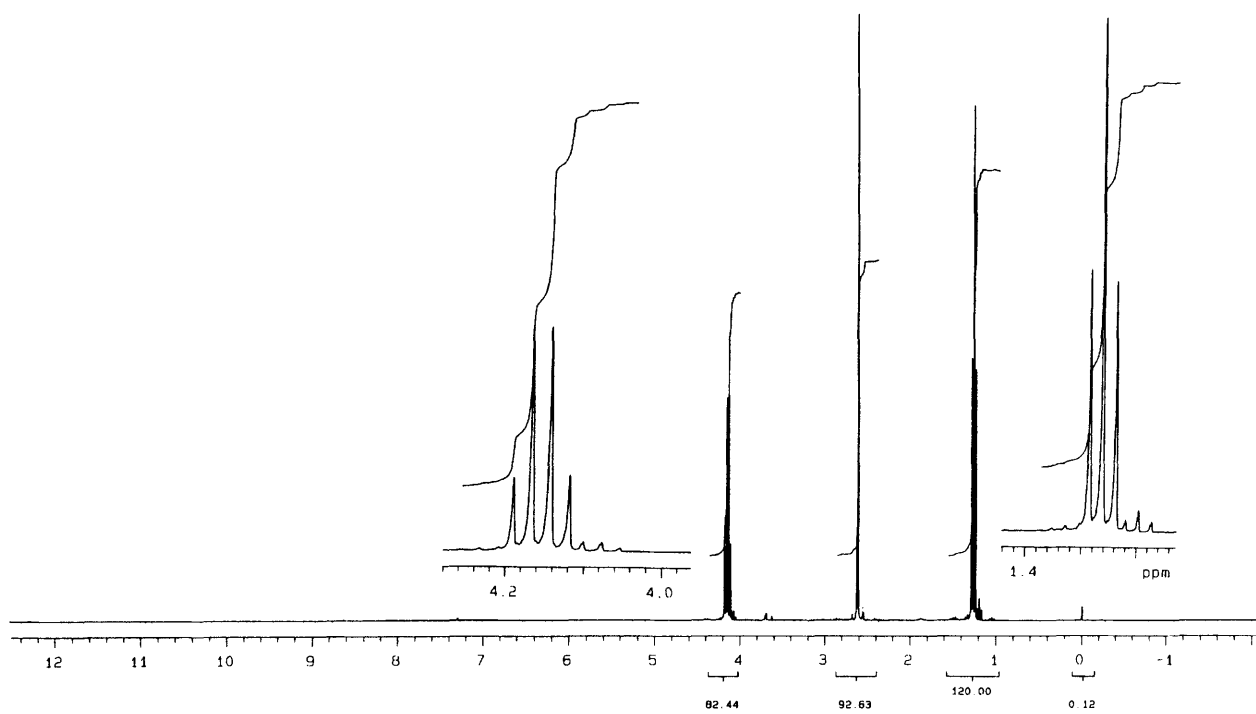
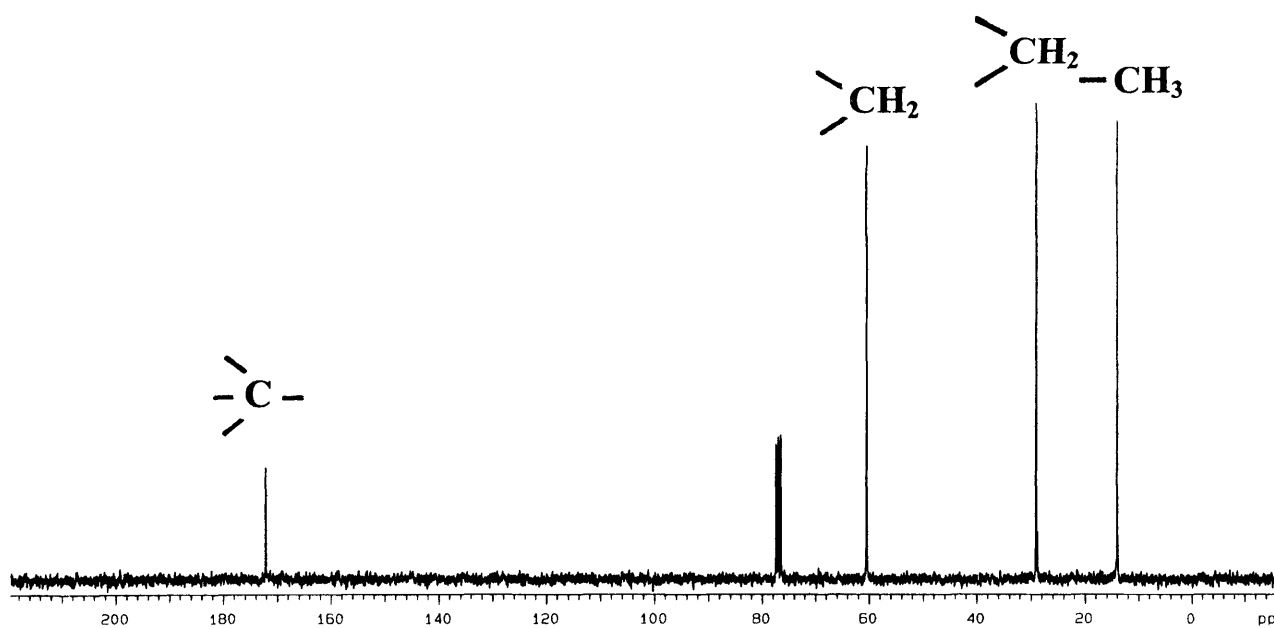
Sample 12.17



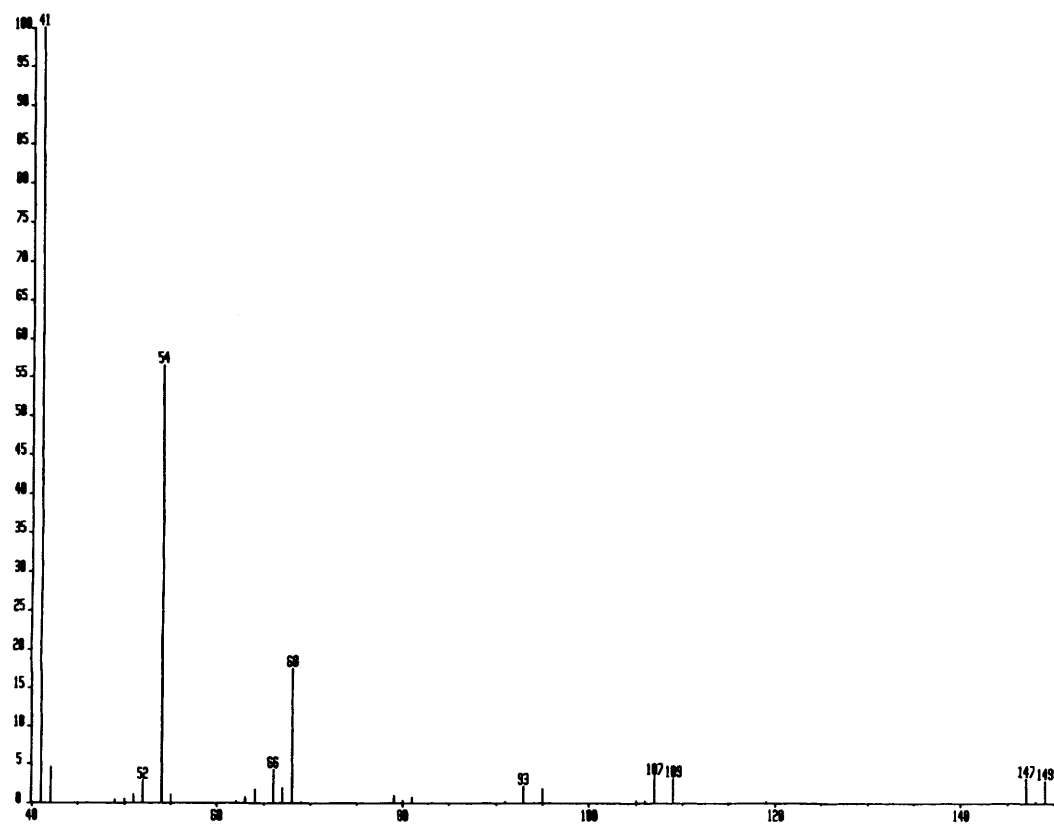
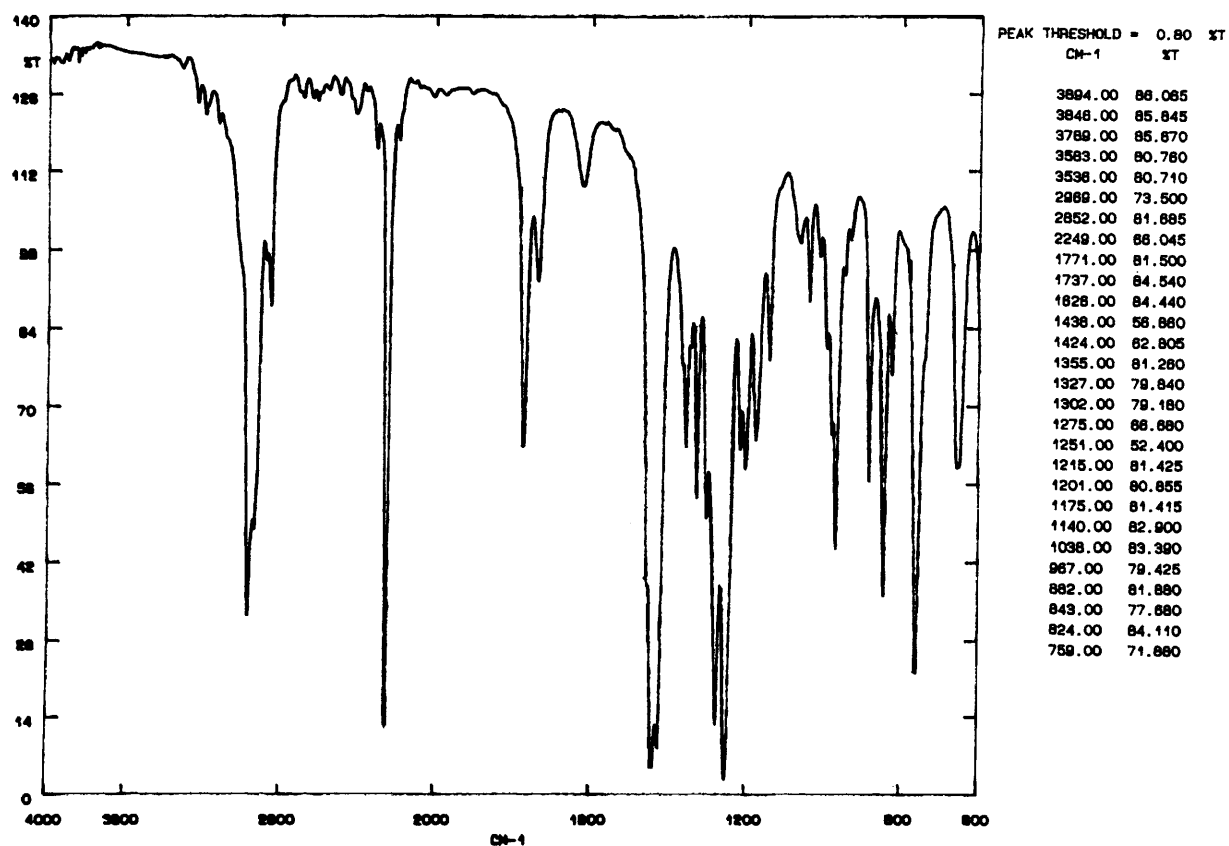
Sample 12.17 Continued



Sample 12.18

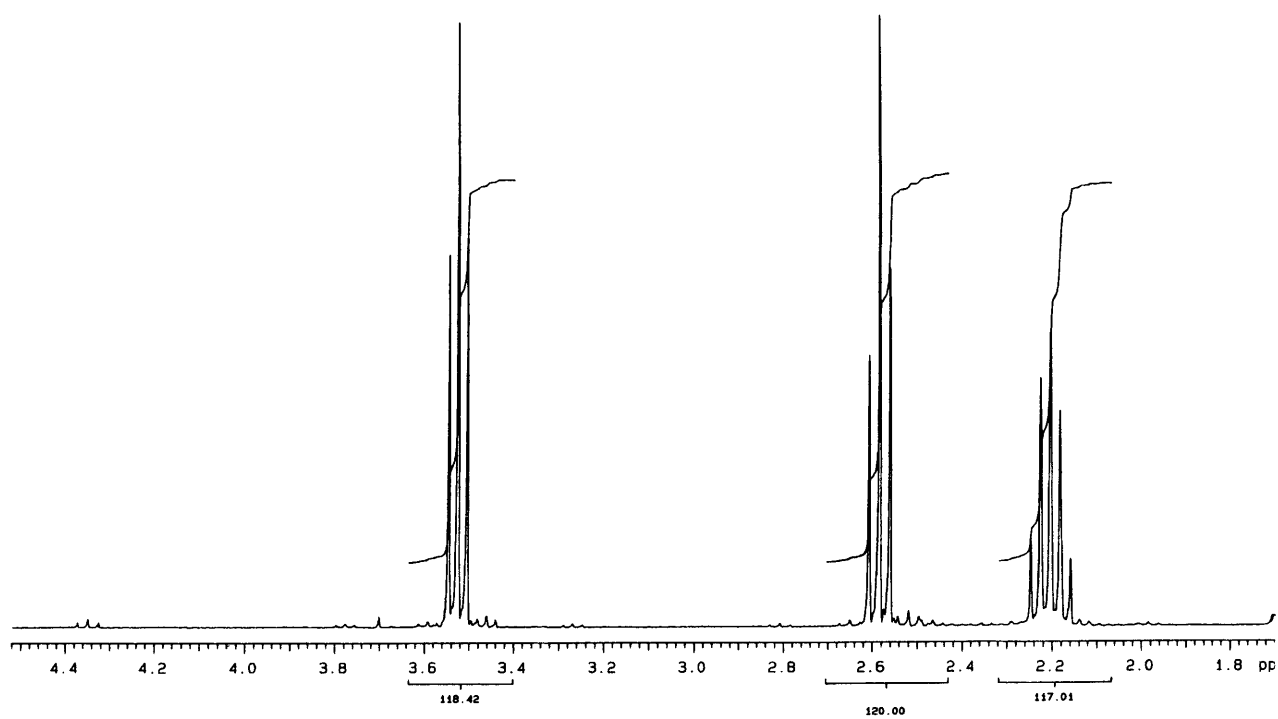
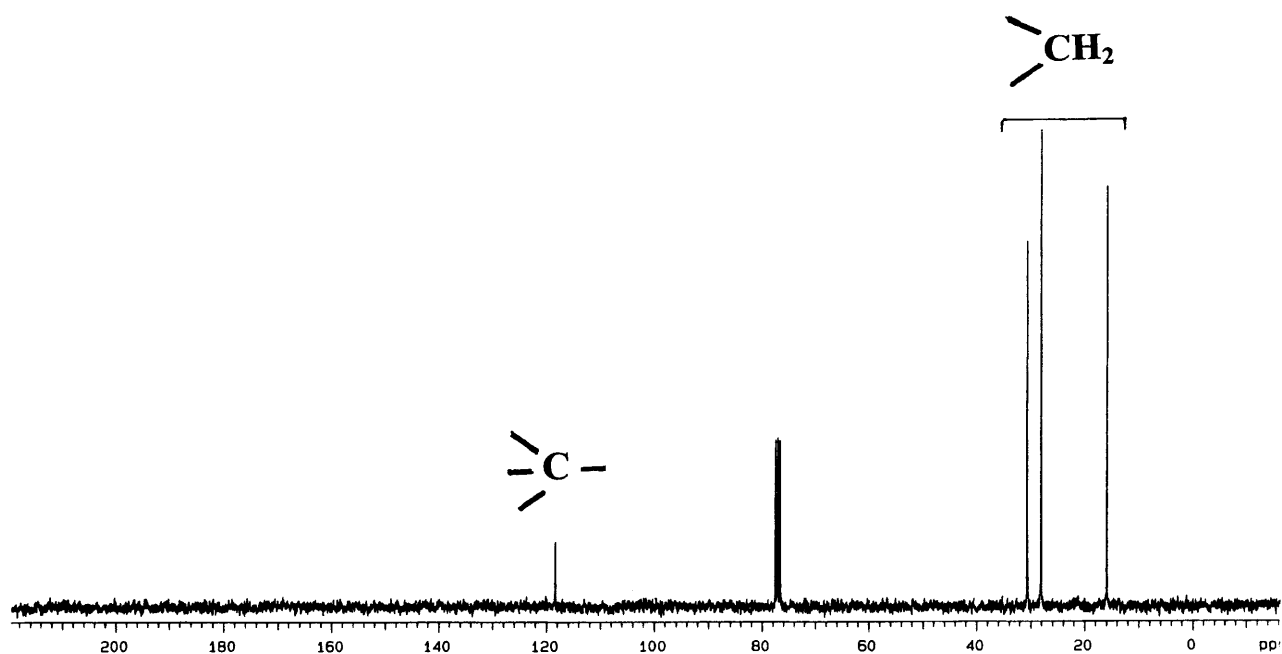


Sample 12.18 Continued

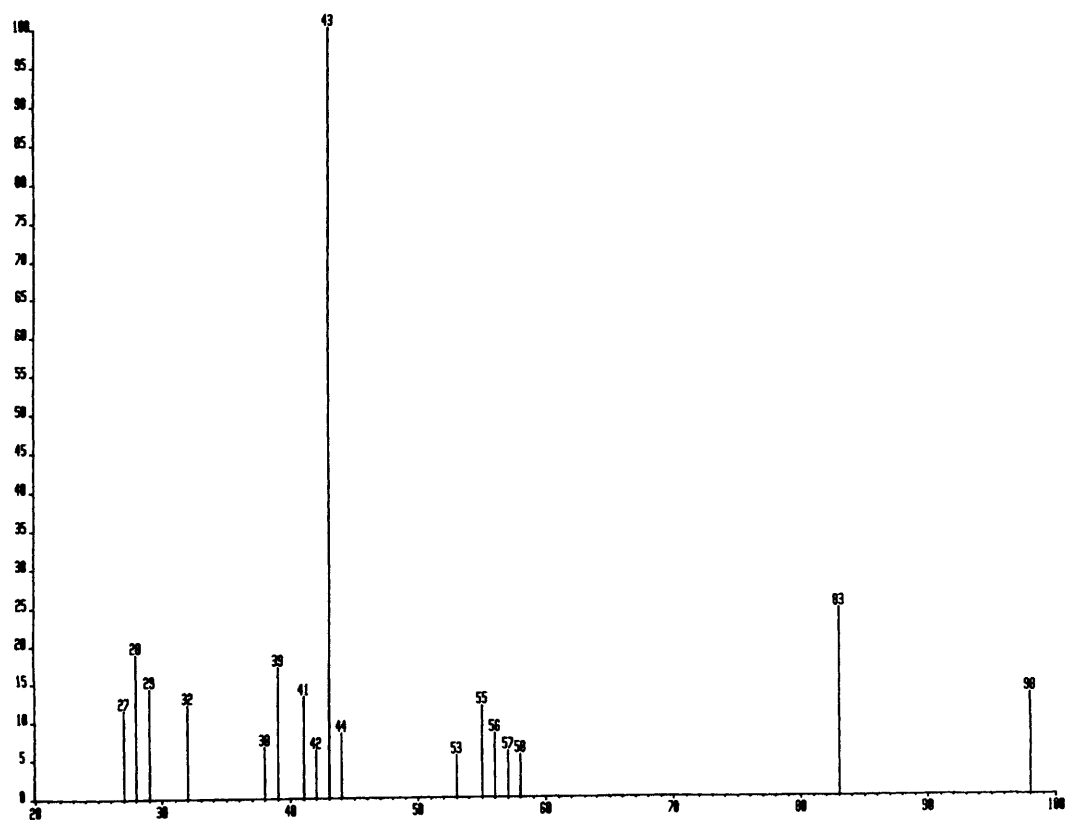
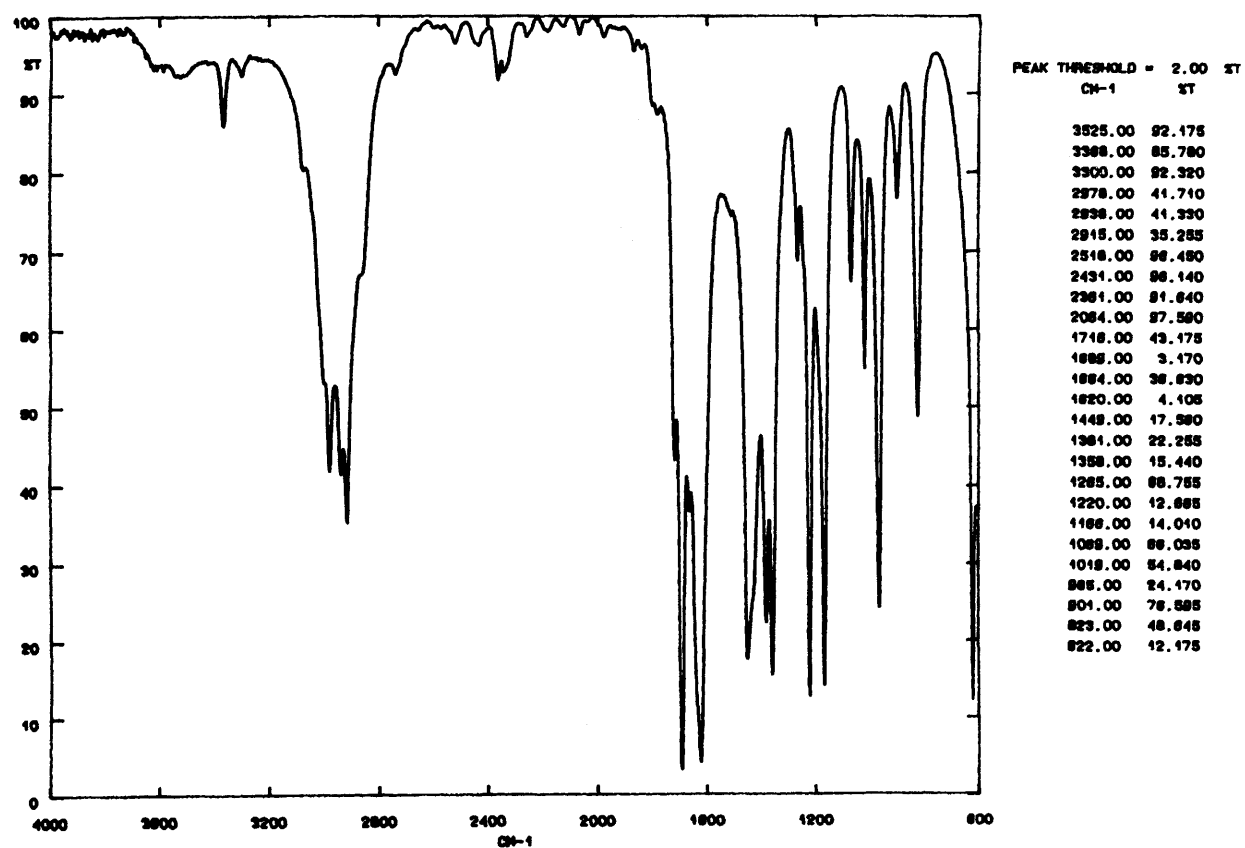


Sample 12.19

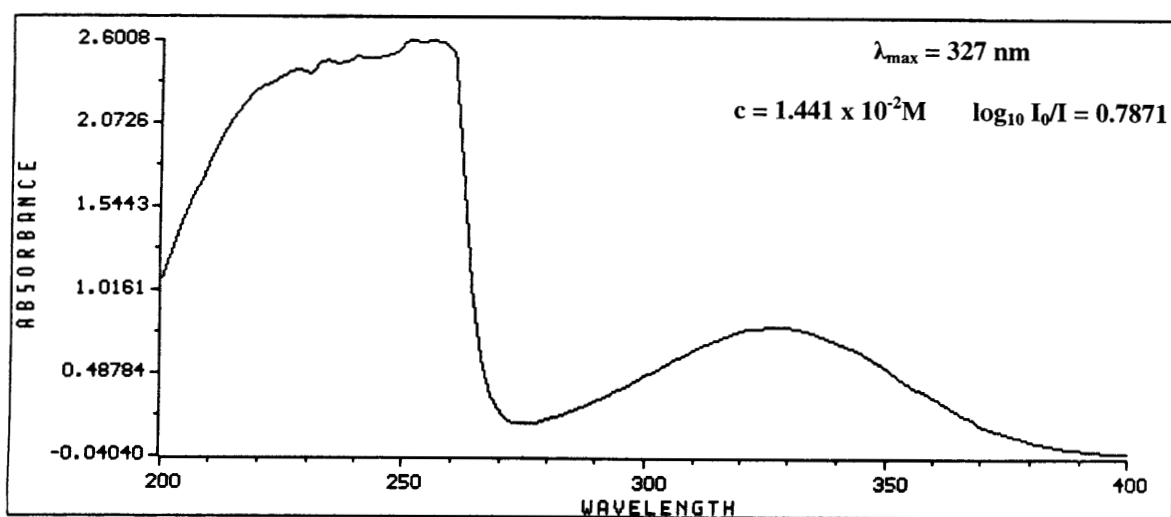
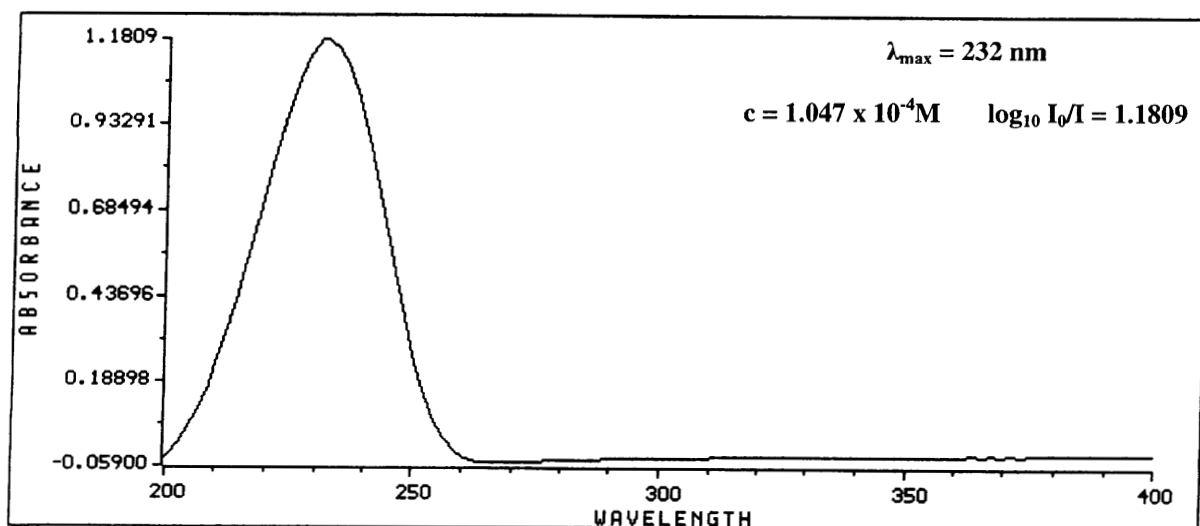




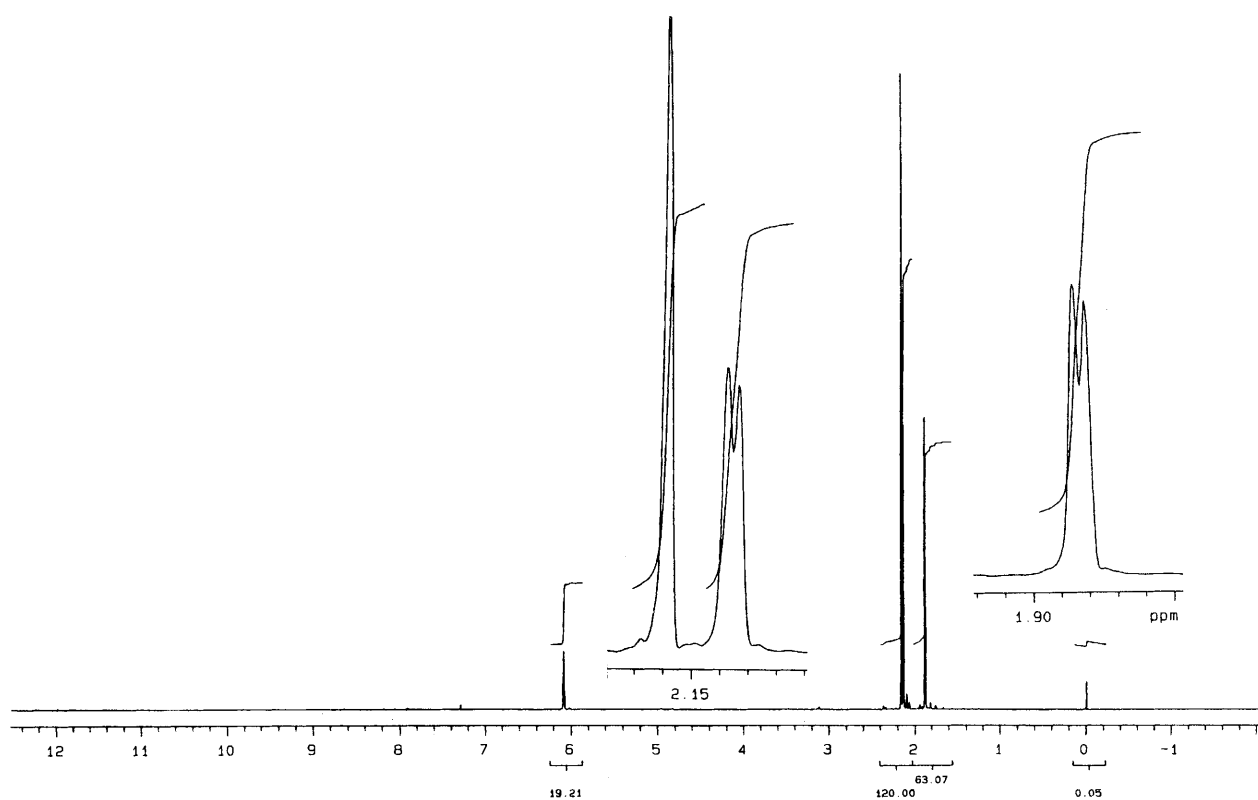
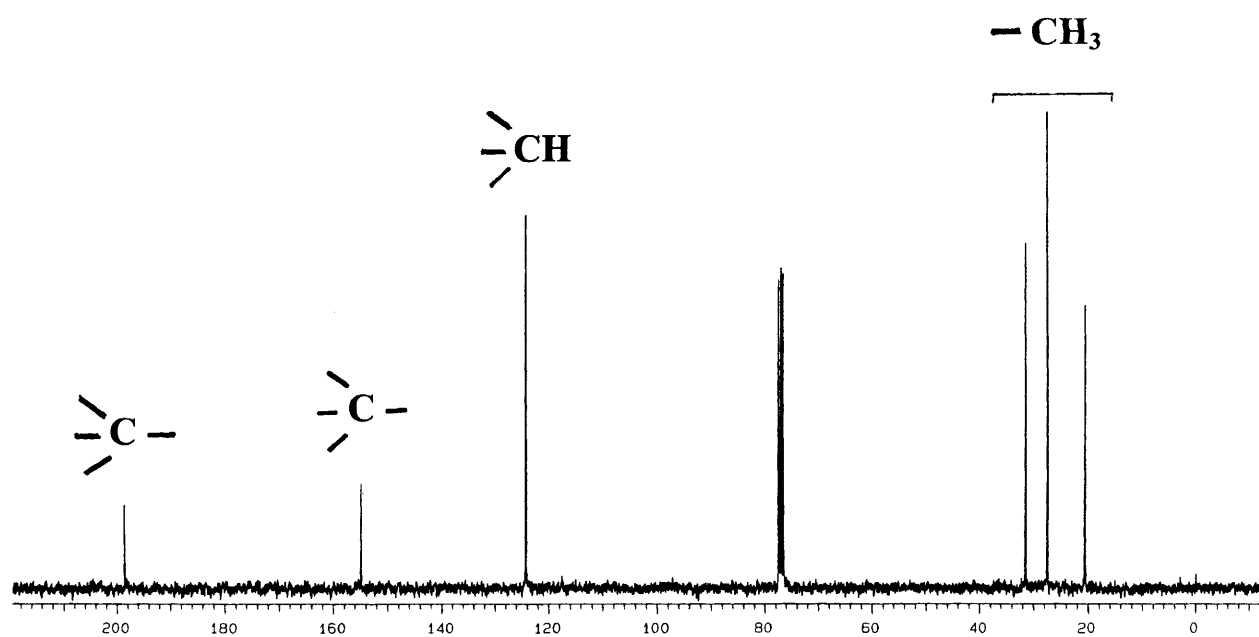
Sample 12.19 Continued



Sample 12.20



Sample 12.20 Continued

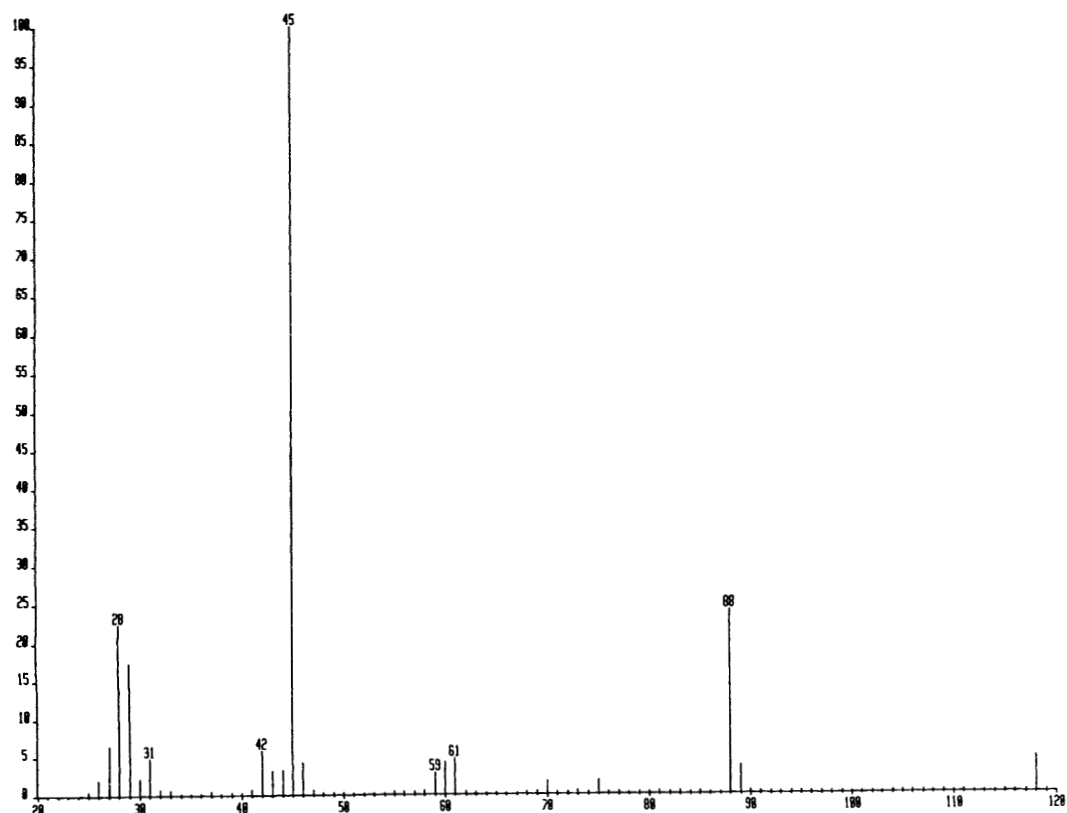
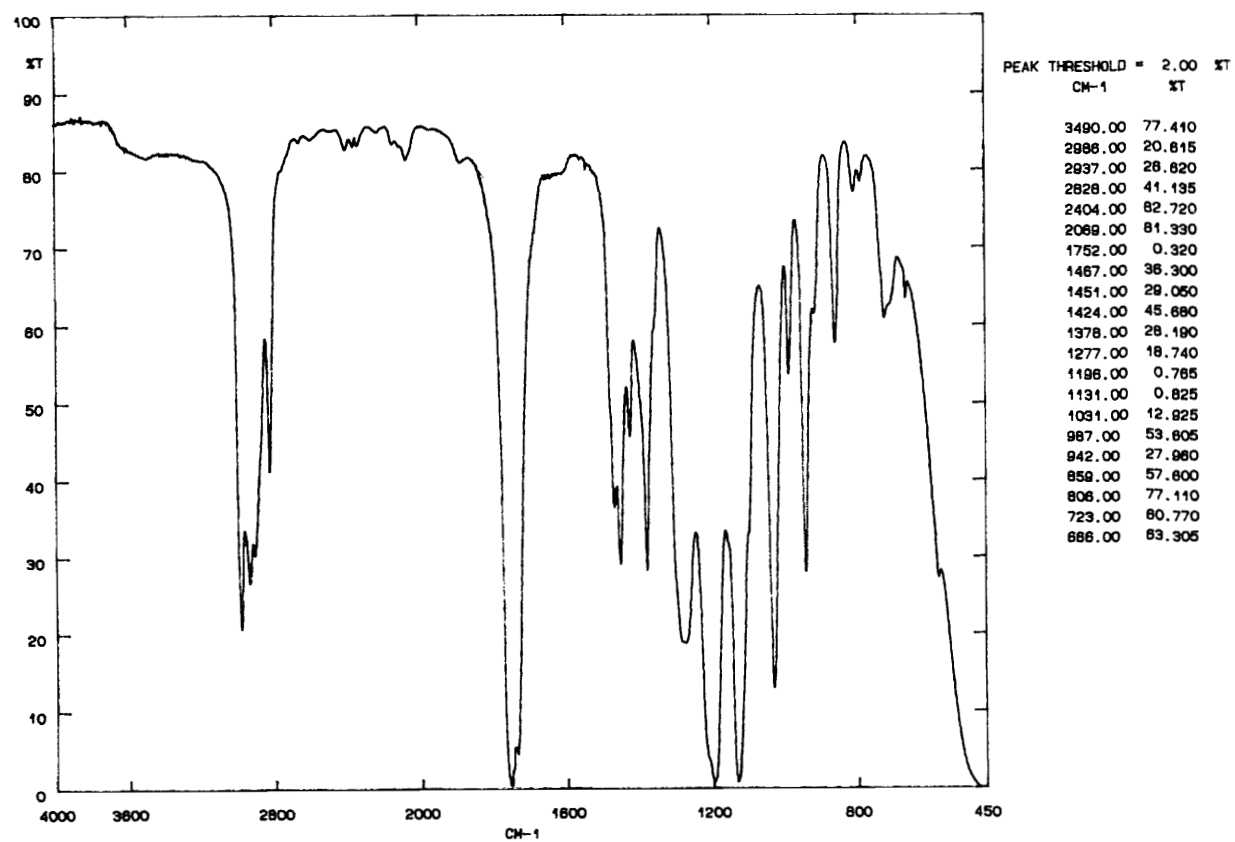


Sample 12.20 Continued

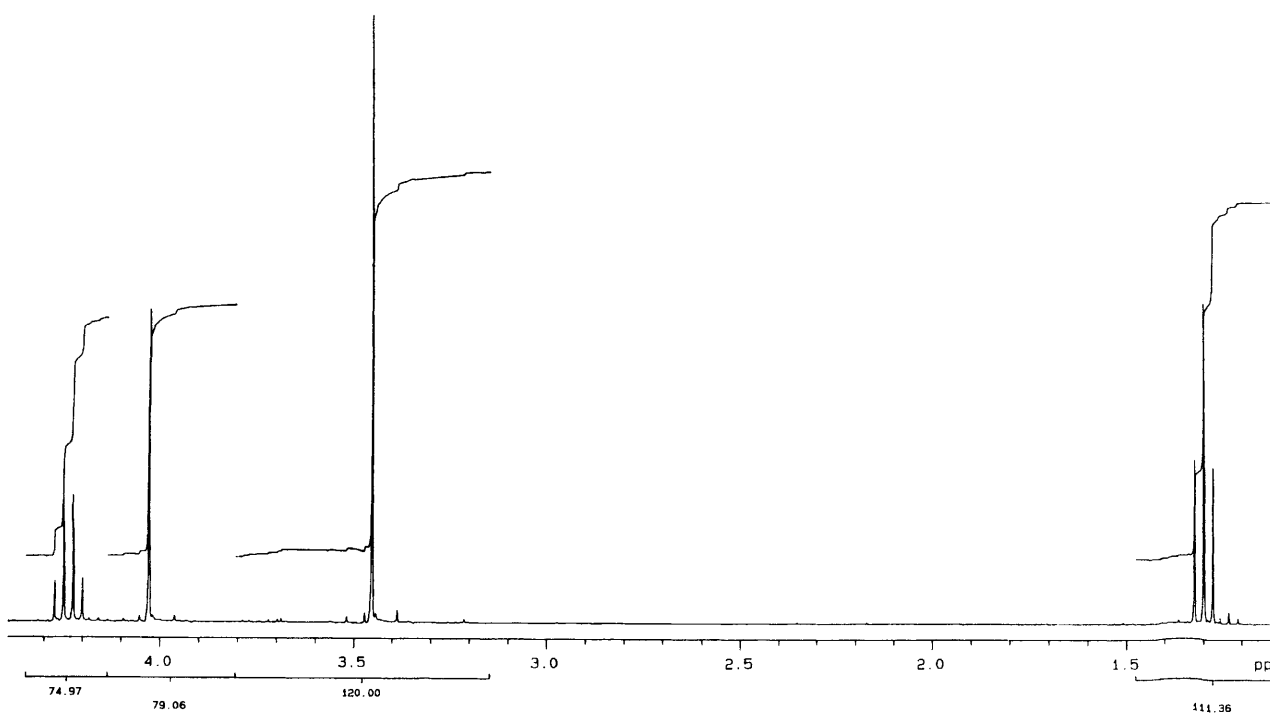
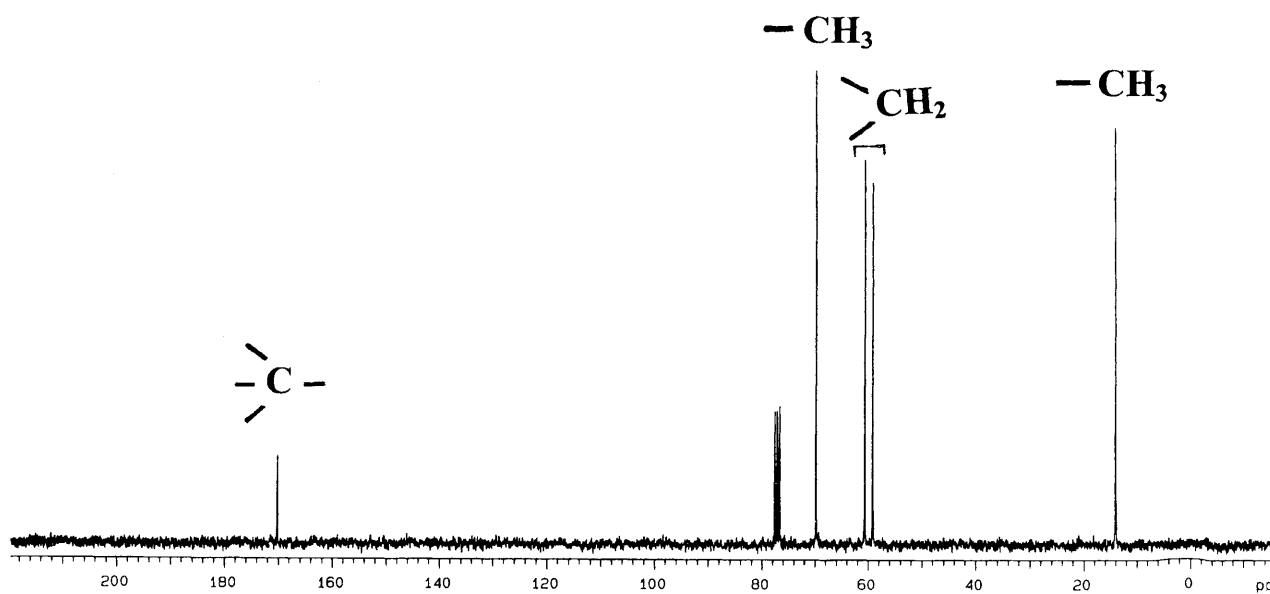
## Difficult Problems in Interpreting Spectra

The spectra in this exercise are more difficult to interpret than those in the previous chapter. This is not the result of supplying spectra of cyclic and rigid systems—you need to go more deeply into  $^1\text{H}$  NMR spectroscopy to solve those. These spectra are more difficult to solve either because they are complex in the sense of having a number of functional groups, or because they come into the category which Professor Abraham once described as ‘deceptively simple’. Three of the samples have NMR spectra which could hardly be simpler, but it does not make them easy to solve. You need to remain aware of the effects of symmetry in considering these spectra, but above all you need some imagination.

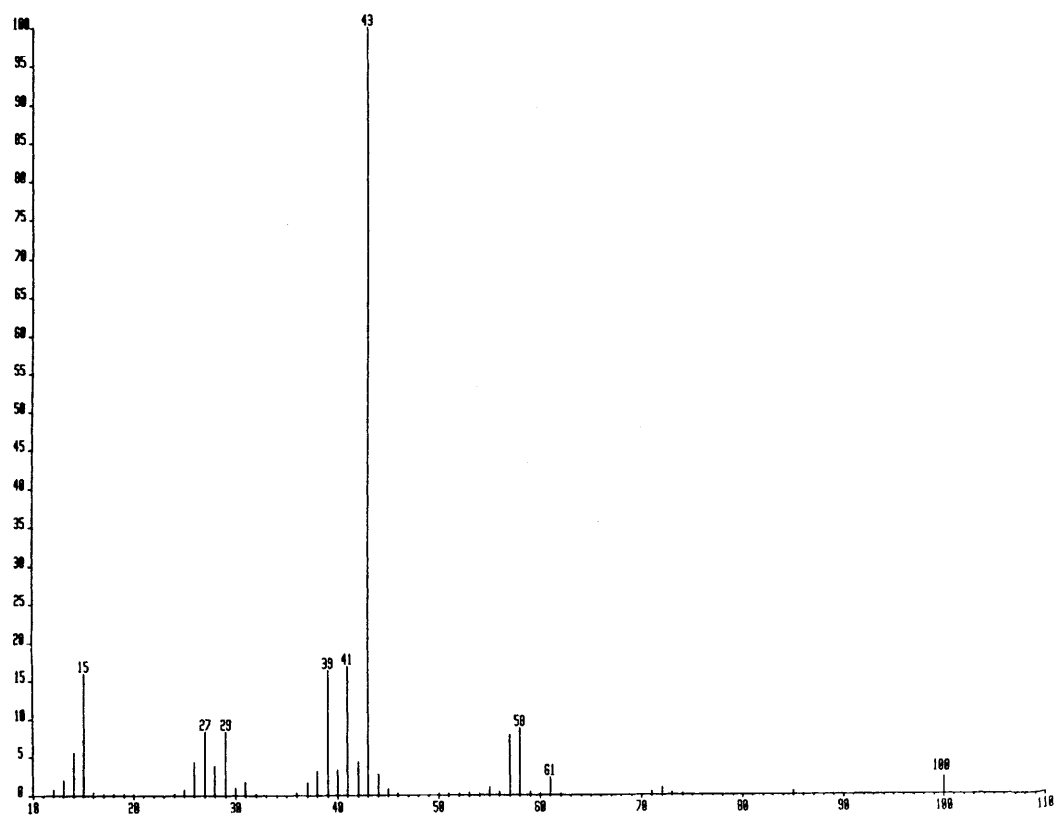
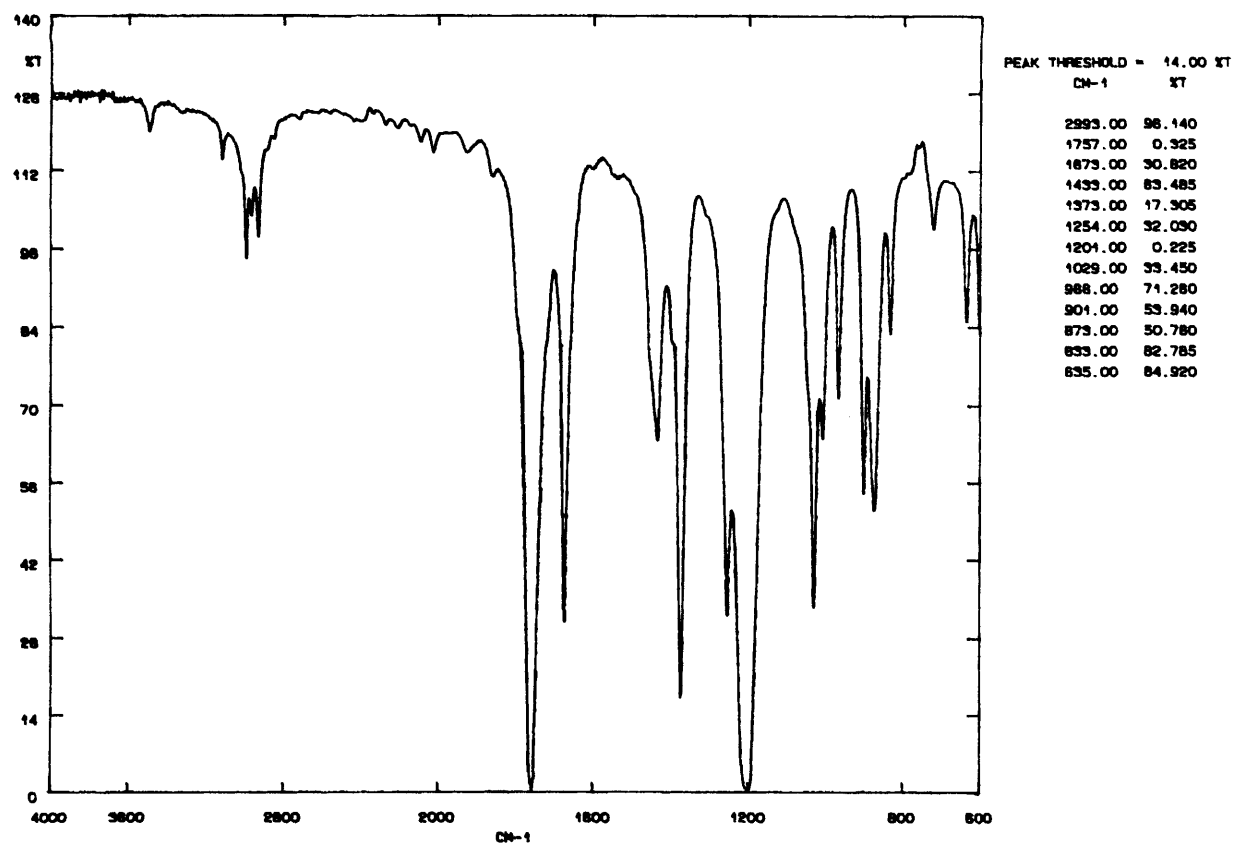
The spectra of 10 samples are provided, some easier than others. All can be solved from the spectra given—one or two of the spectra in fact are hardly necessary, which is exactly the situation you will find when working at the bench.



Sample 13.1

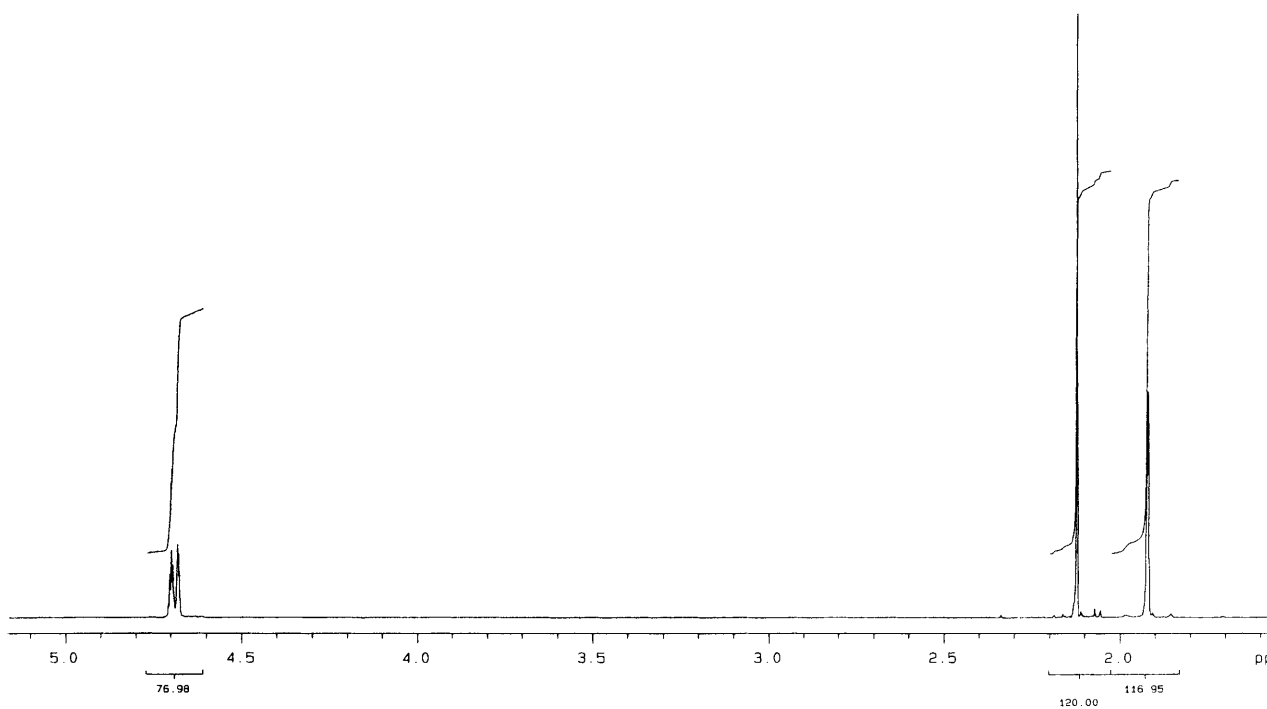
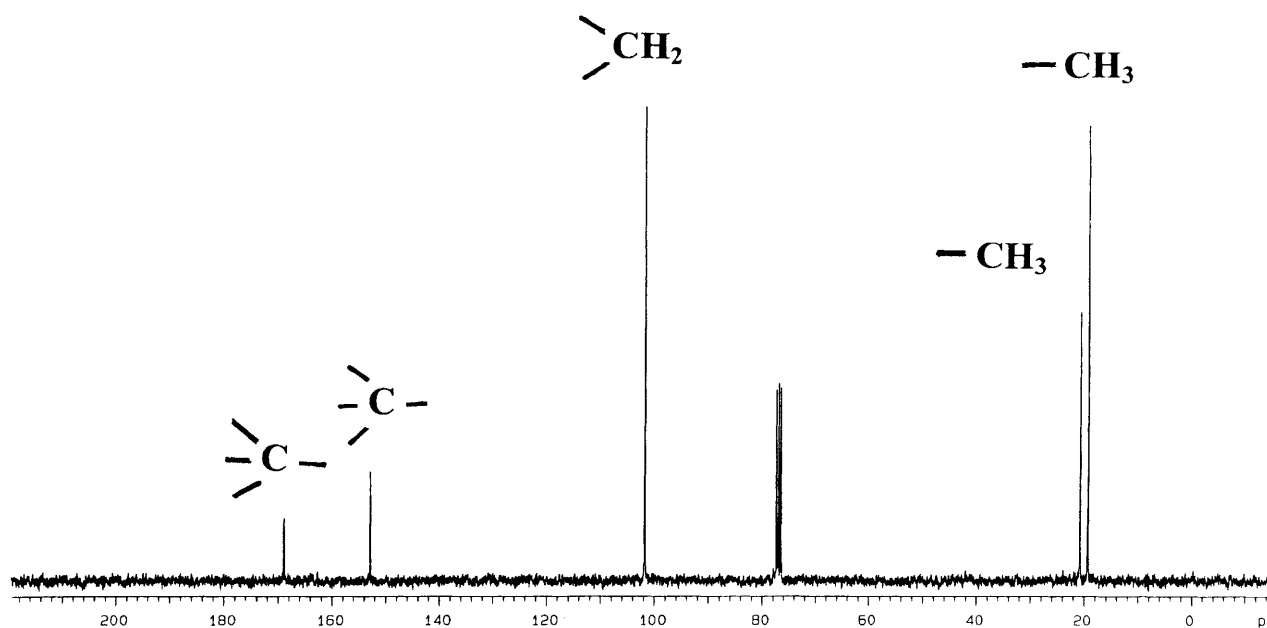


Sample 13.1 Continued

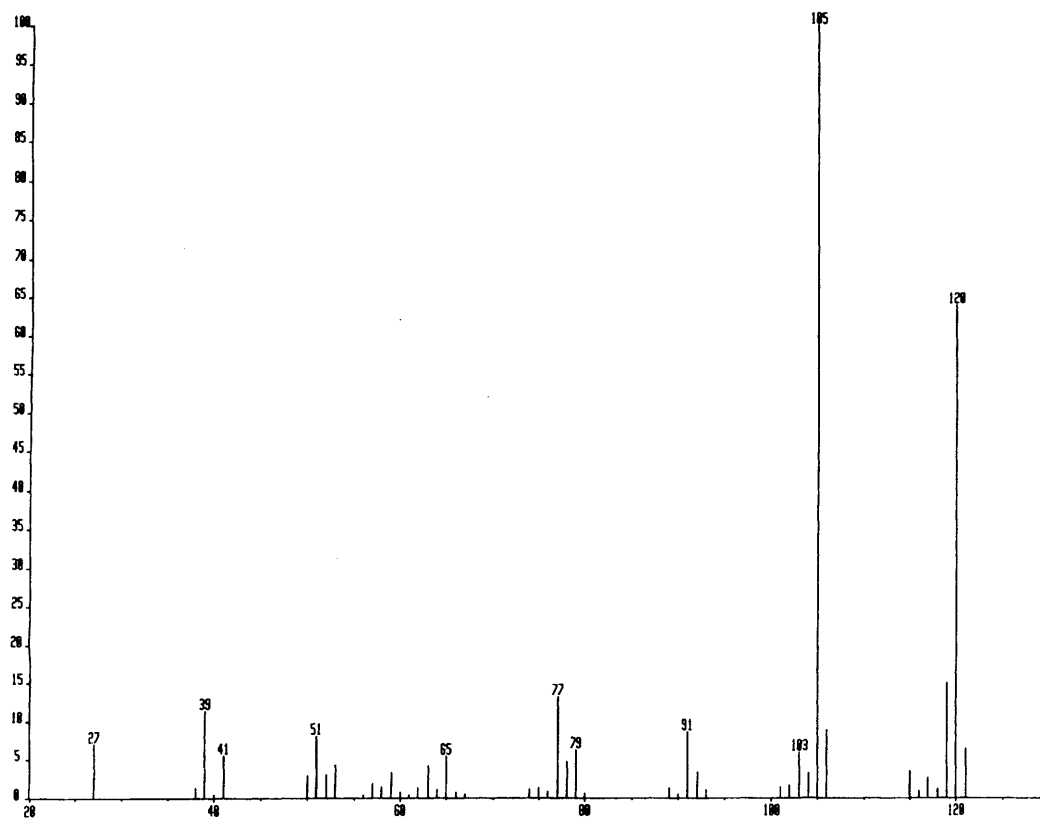
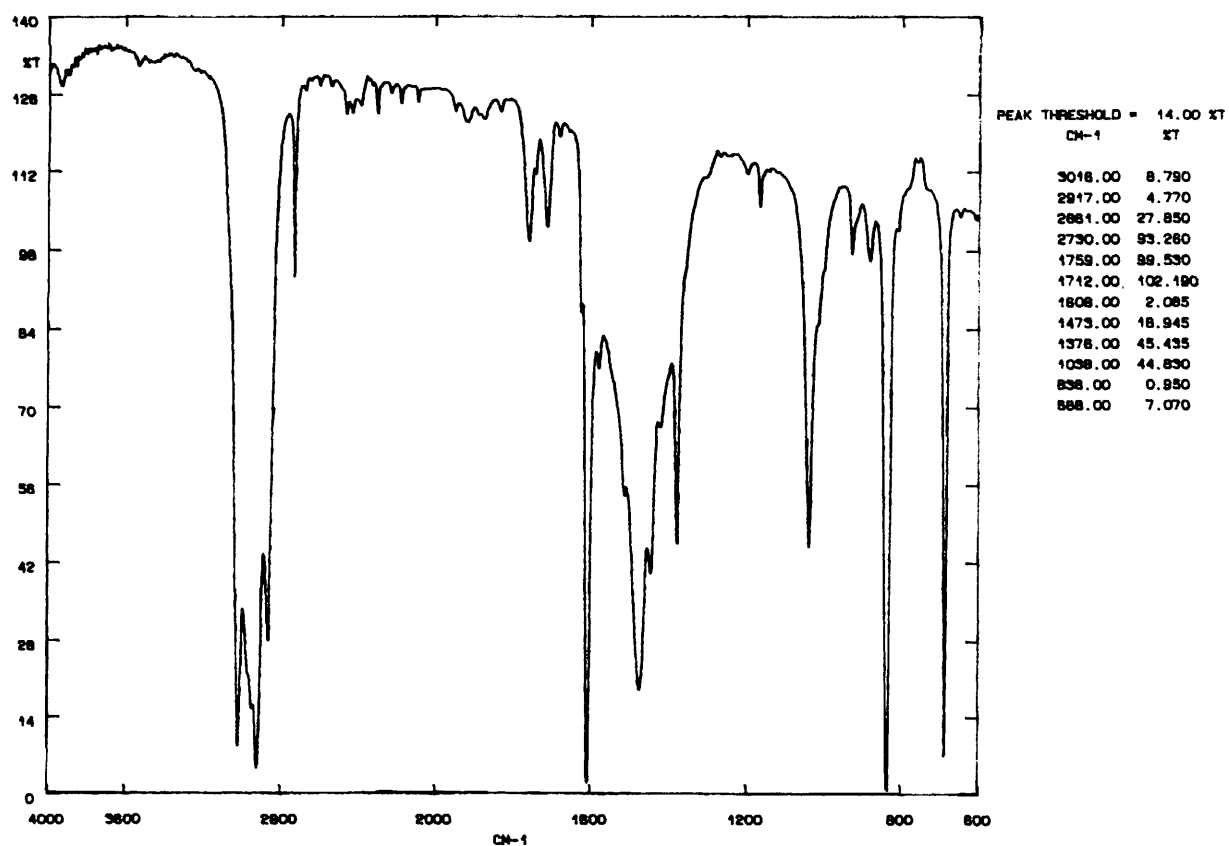


Sample 13.2

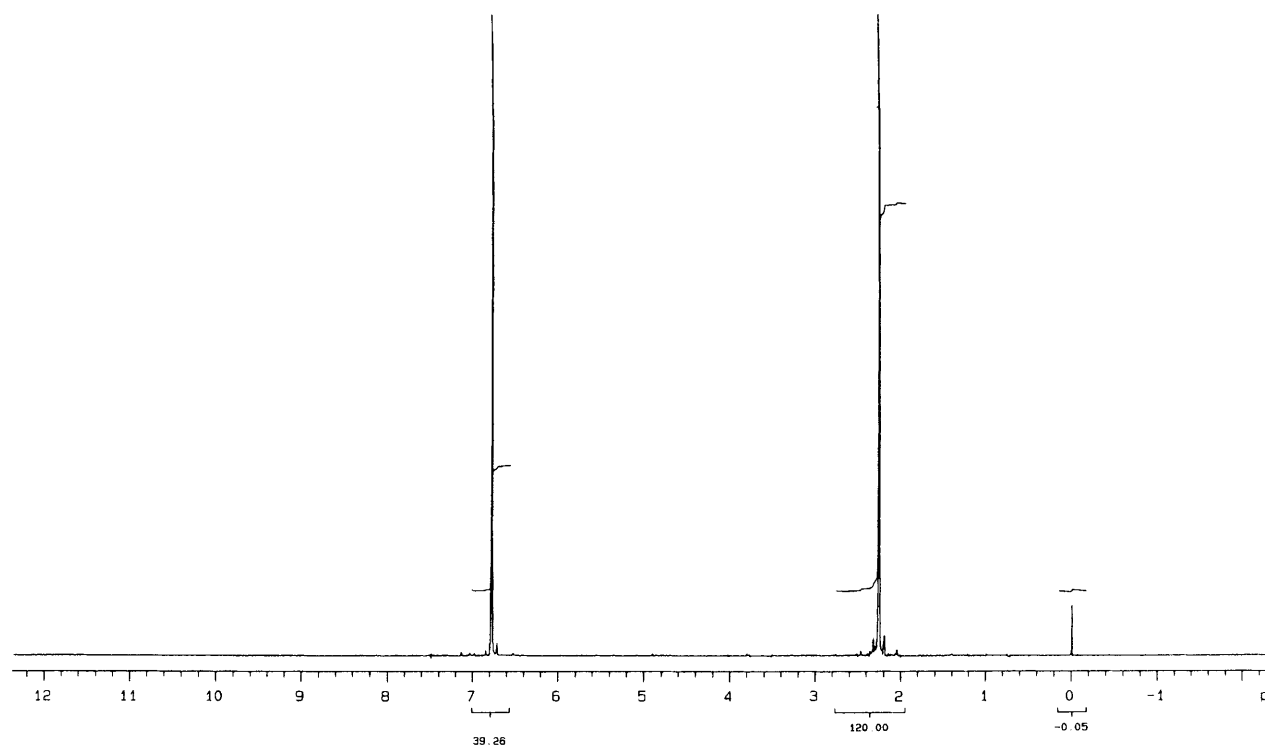
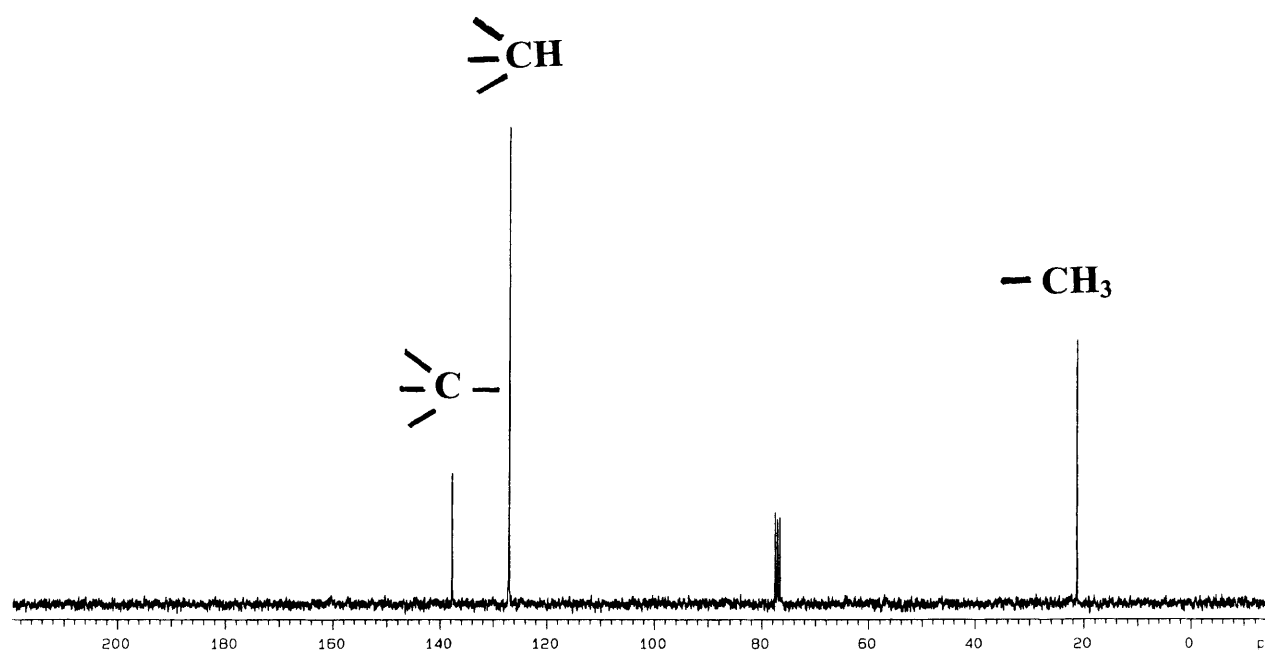




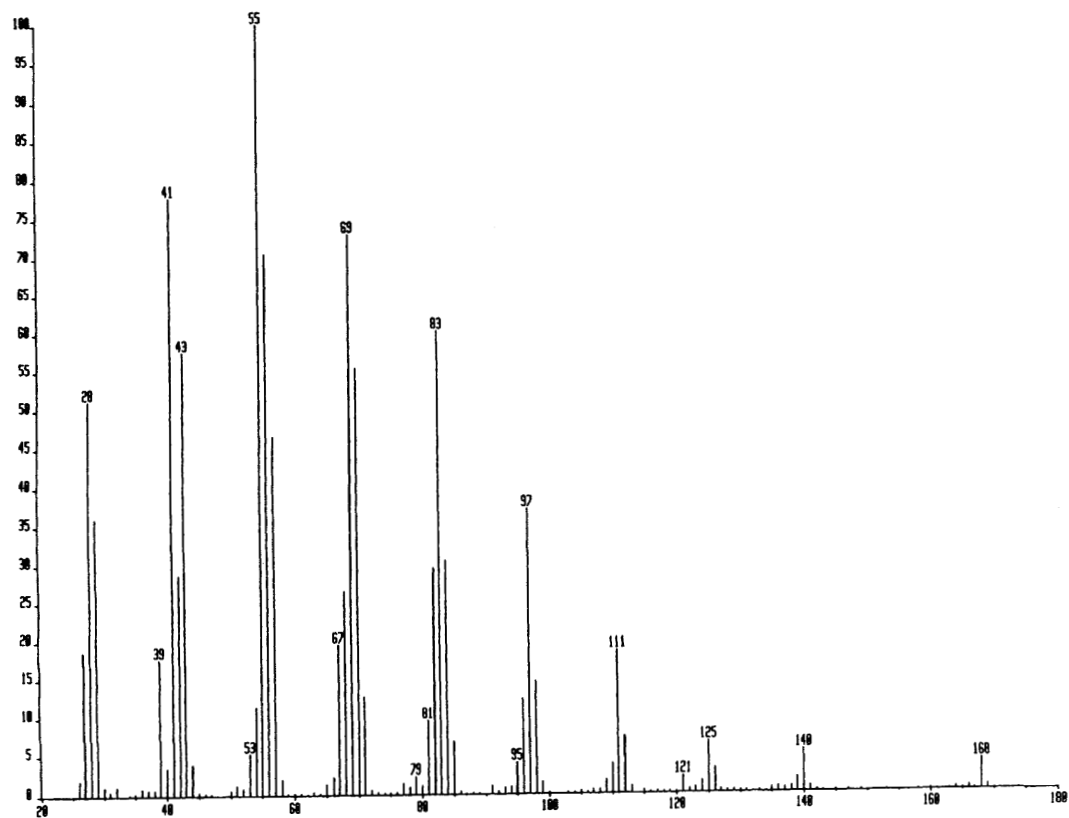
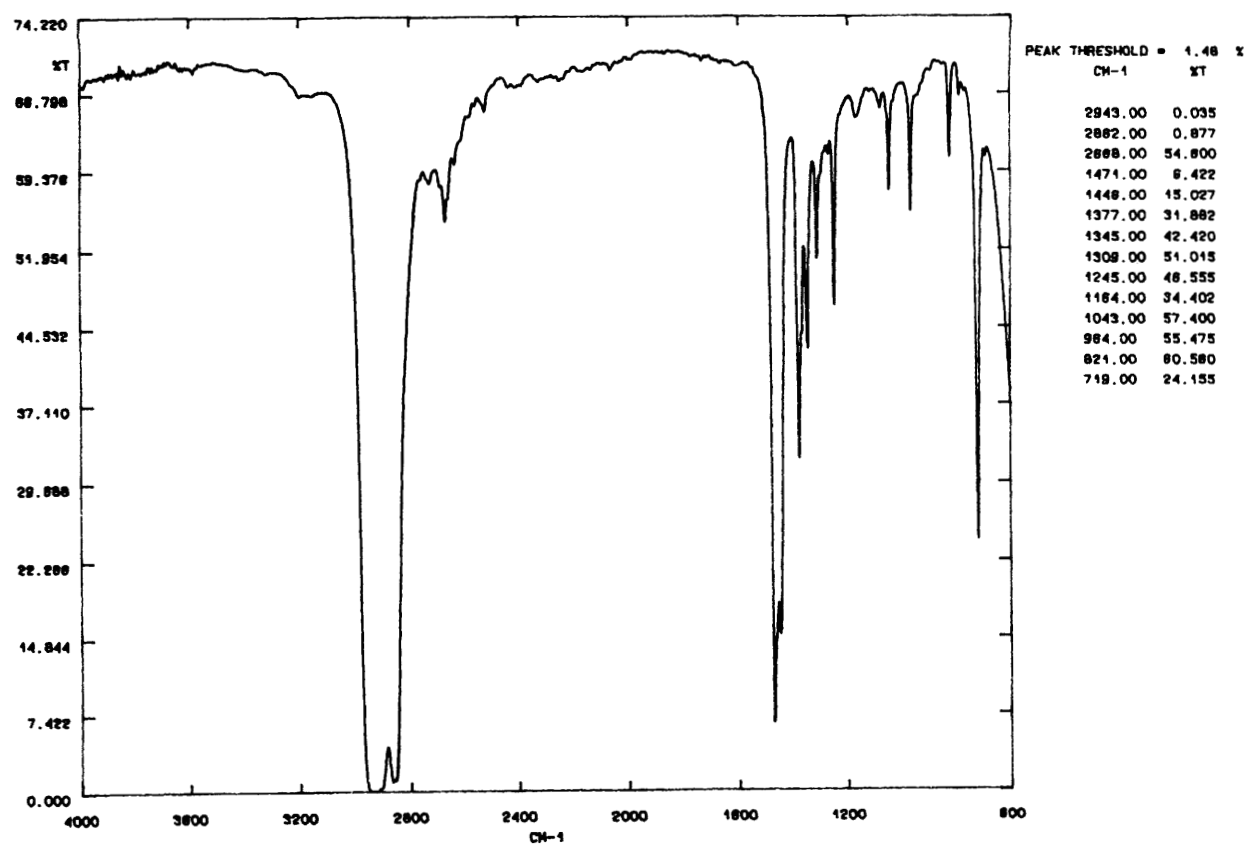
Sample 13.2 Continued



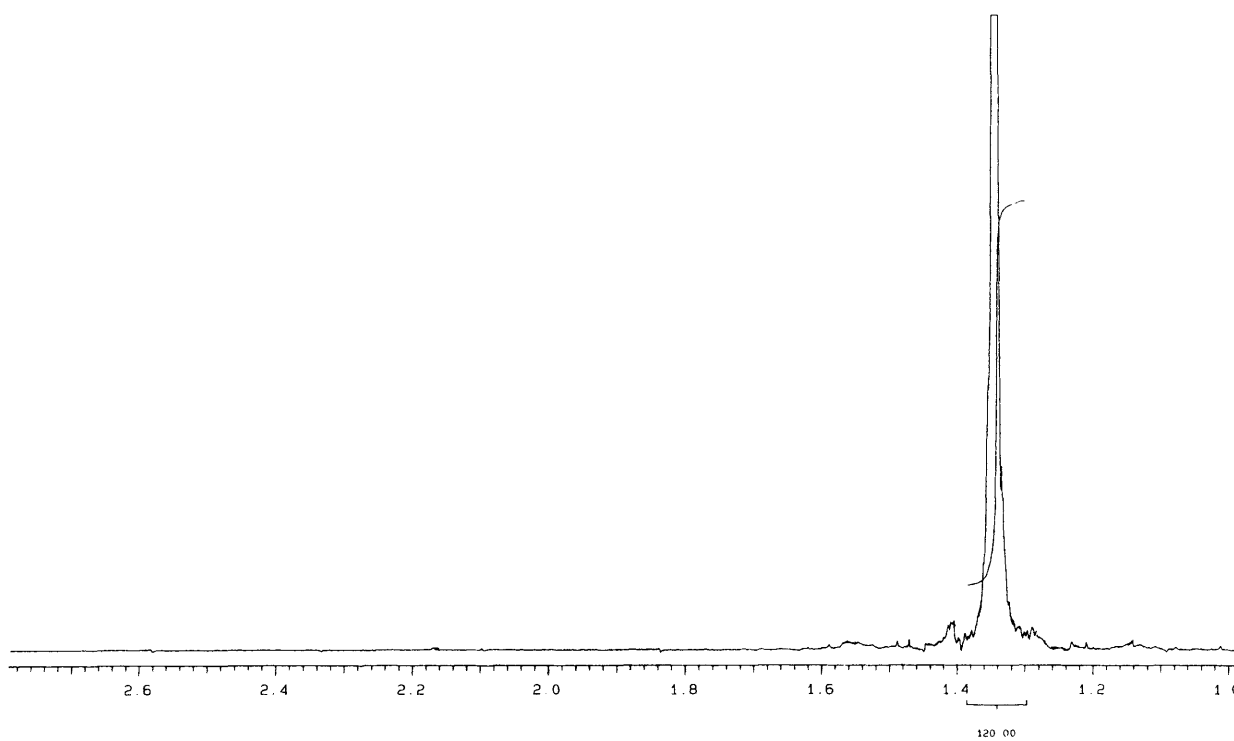
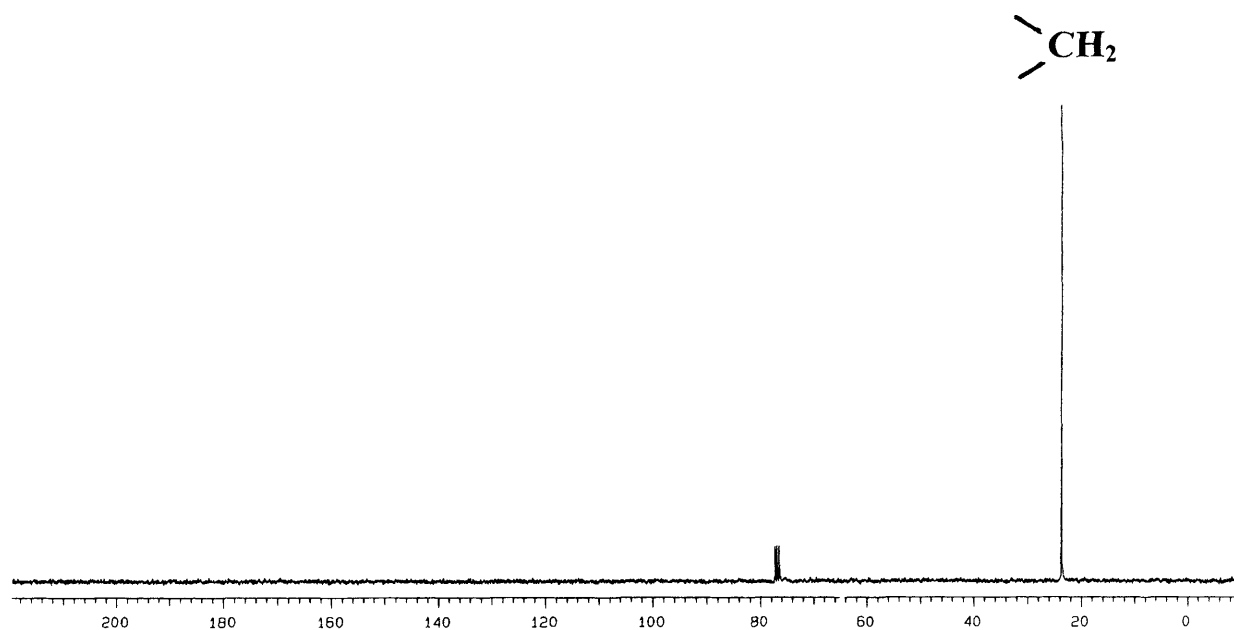
Sample 13.3



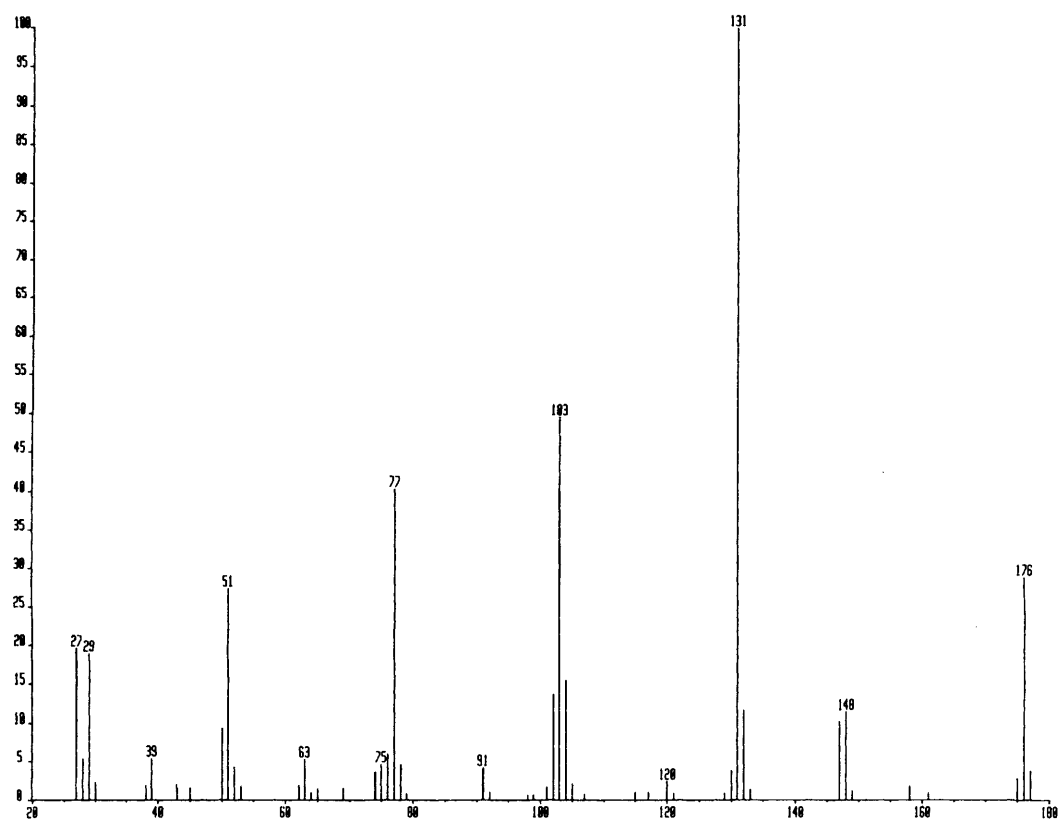
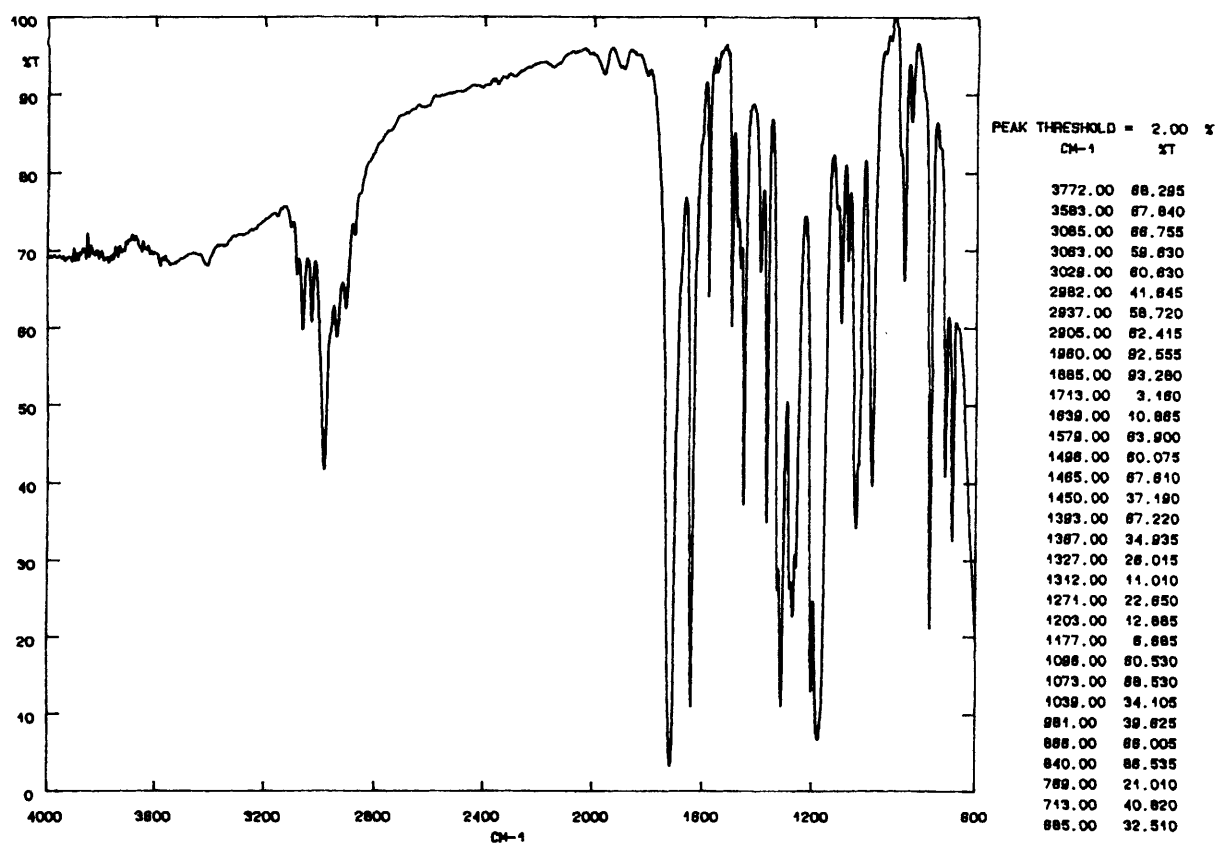
Sample 13.3 Continued



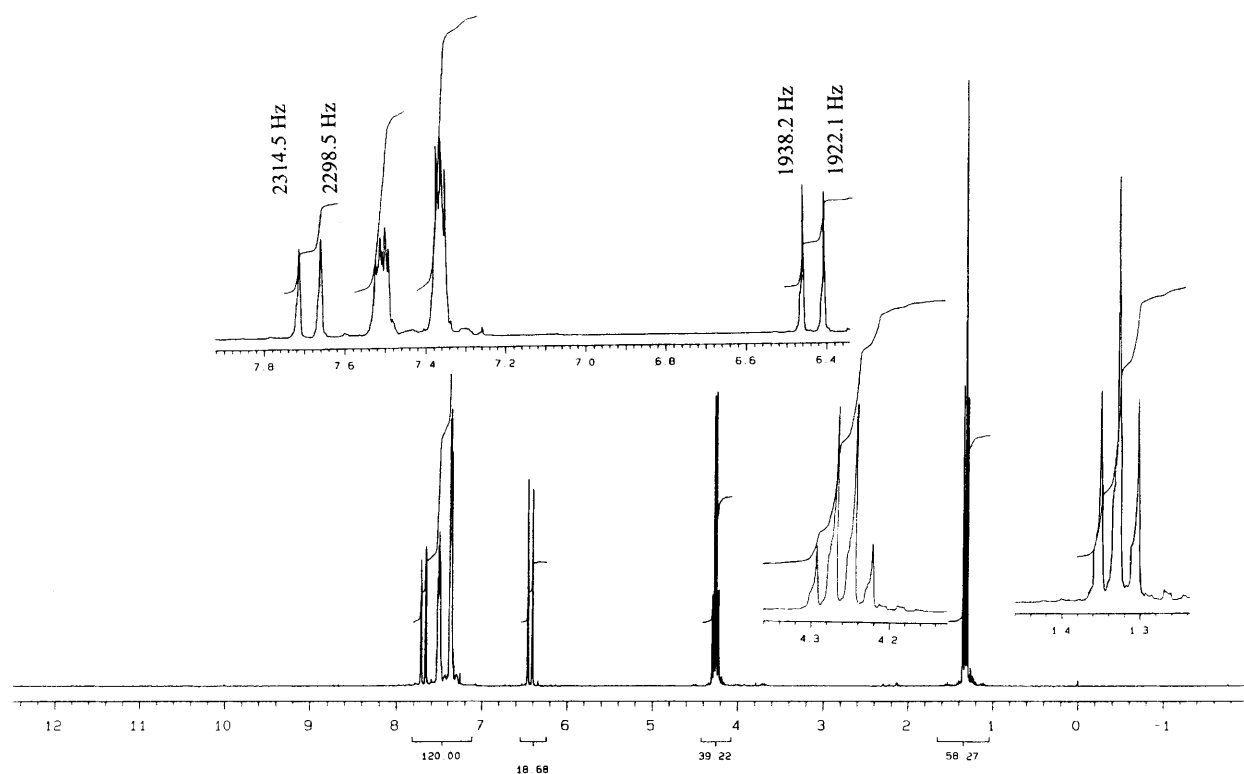
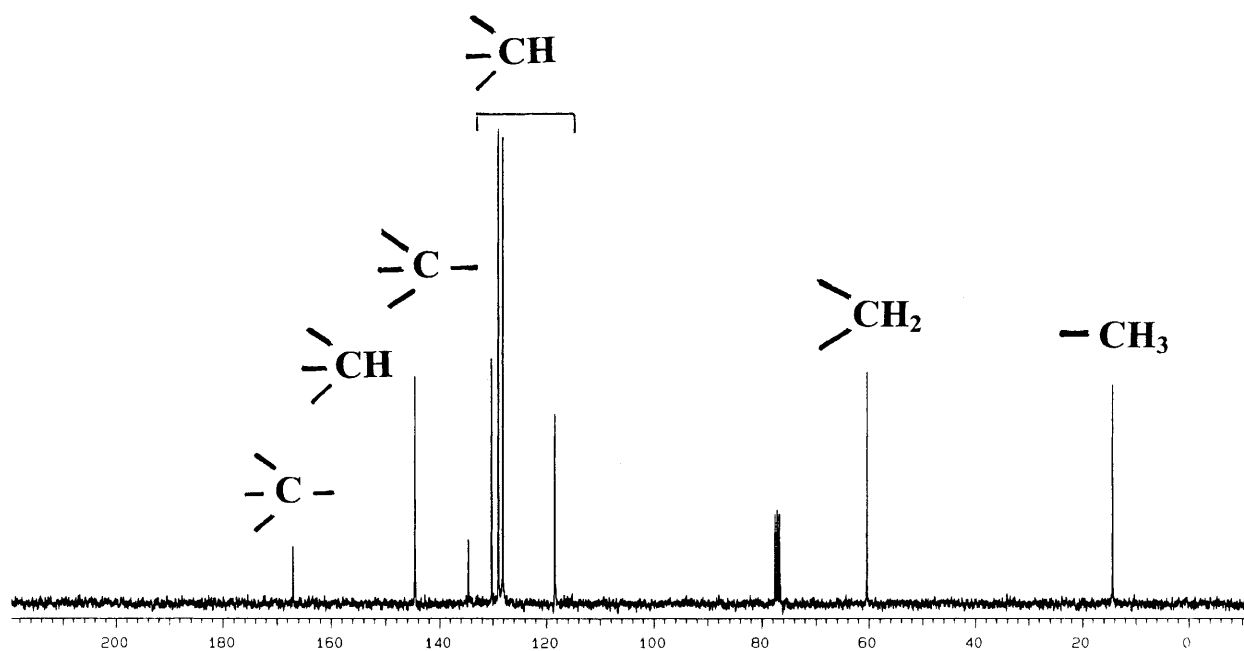
Sample 13.4



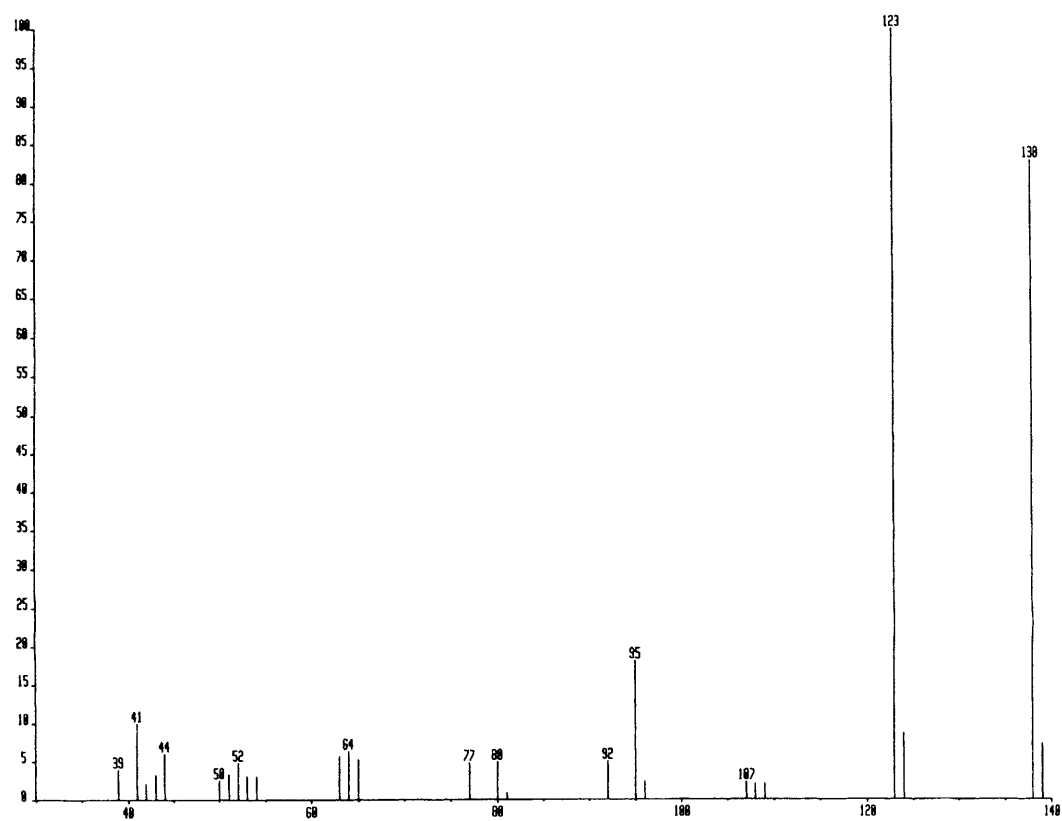
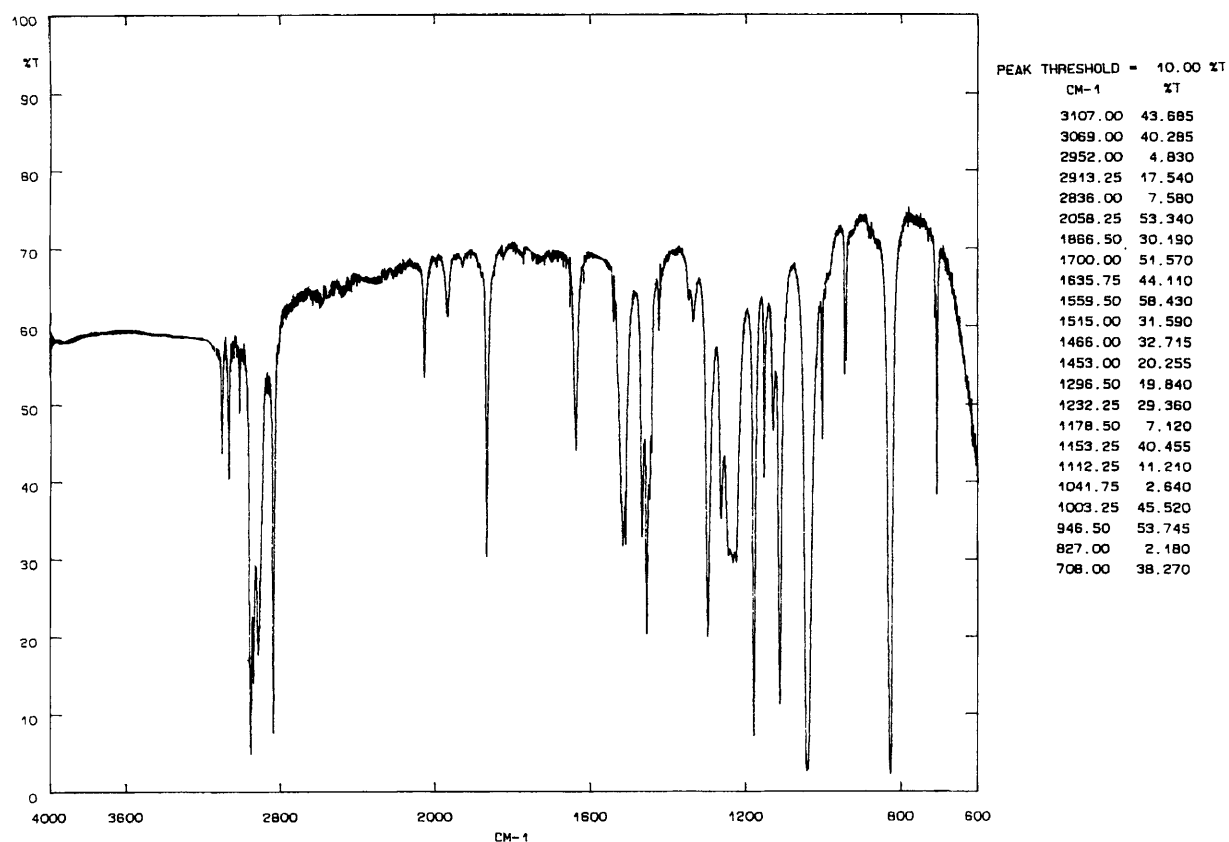
Sample 13.4 Continued



Sample 13.5

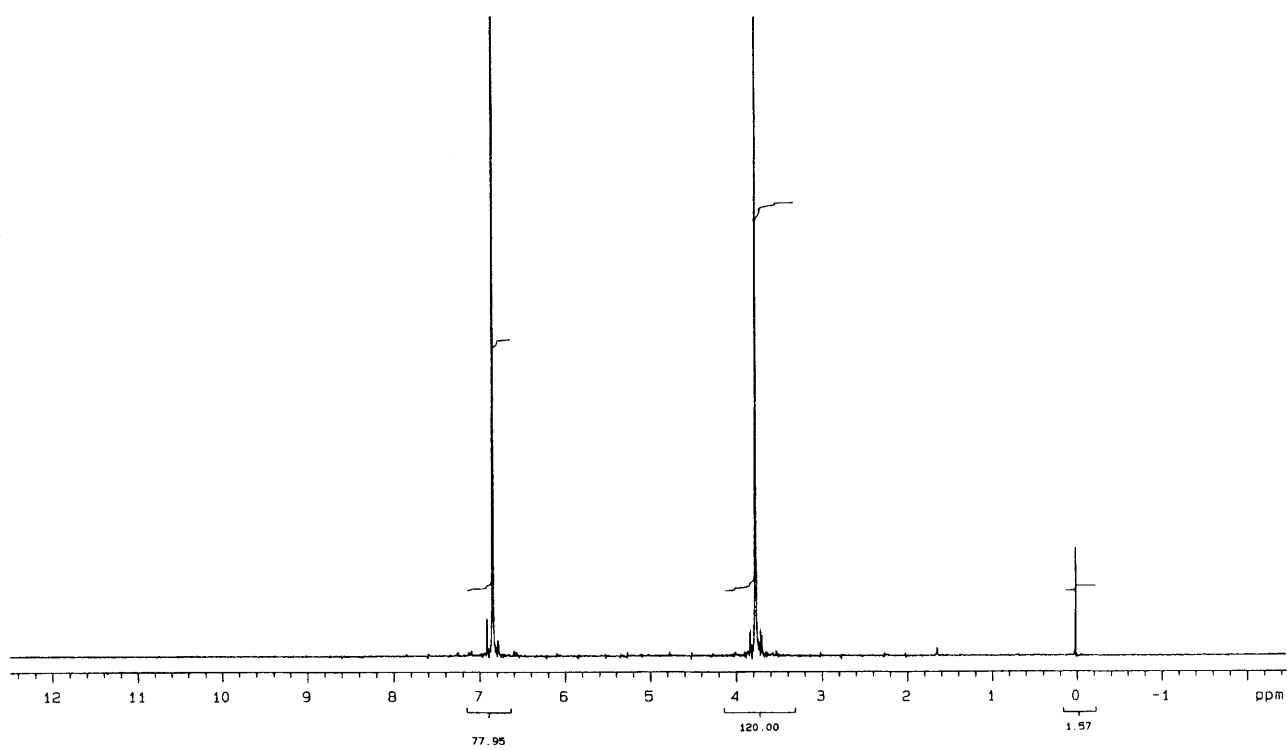
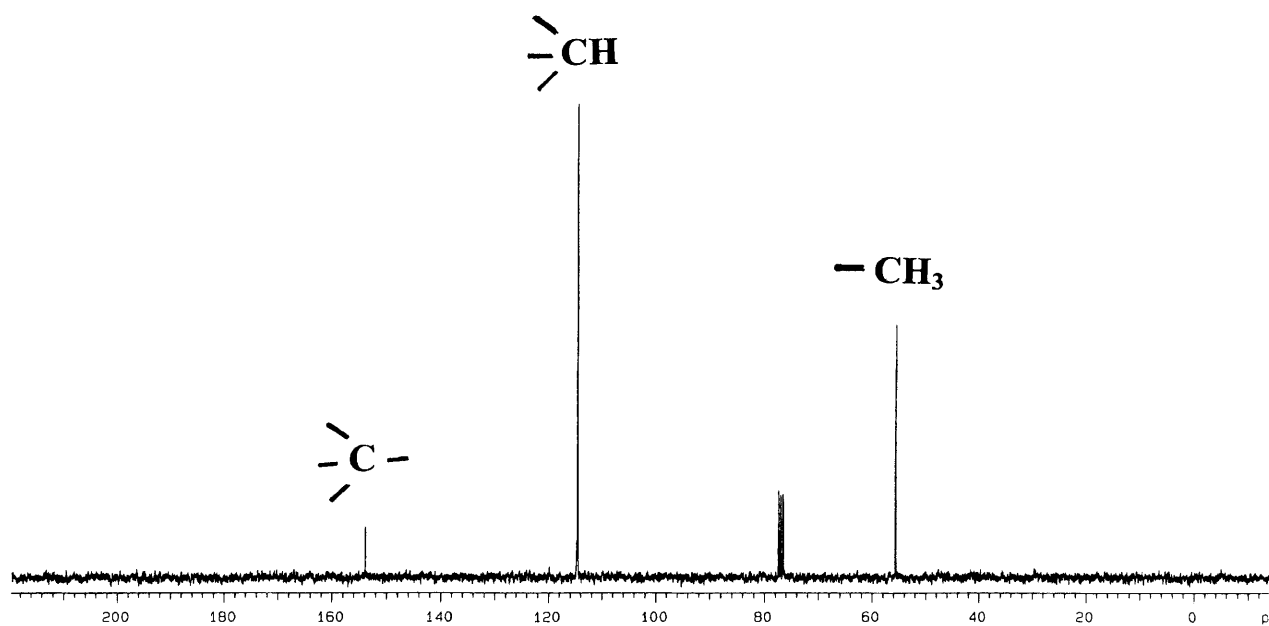


Sample 13.5 Continued

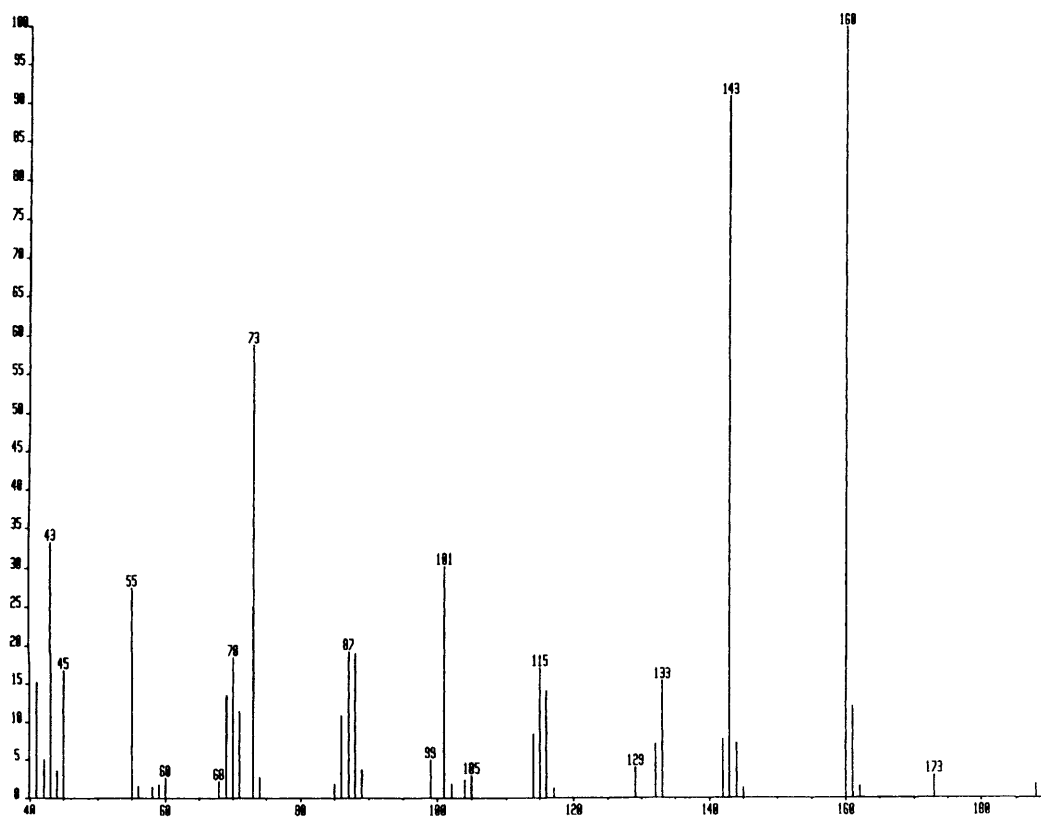
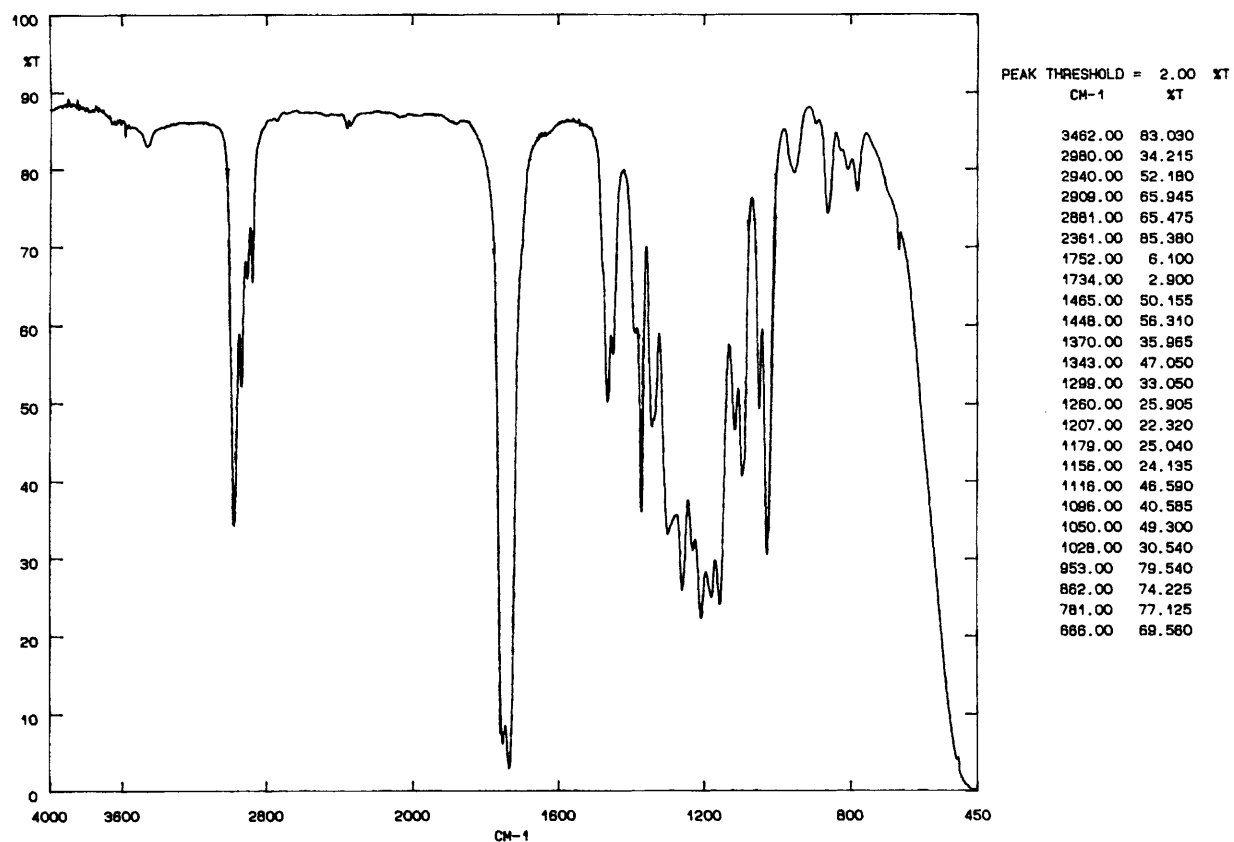


Sample 13.6

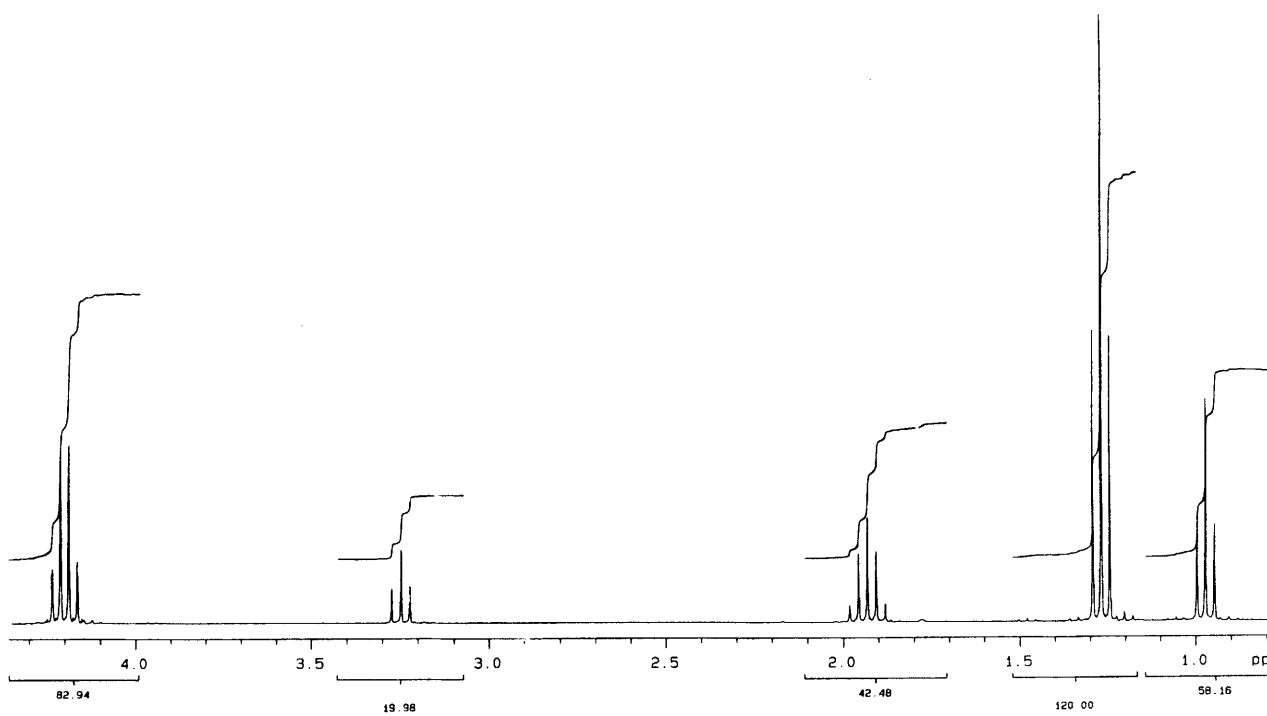
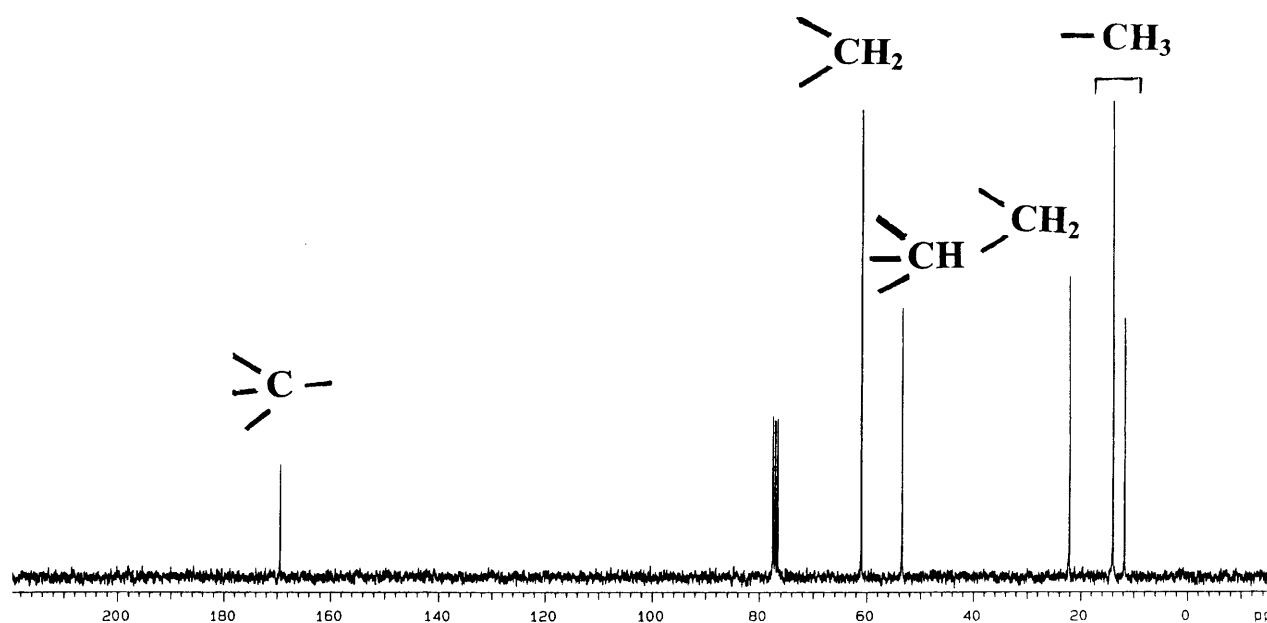




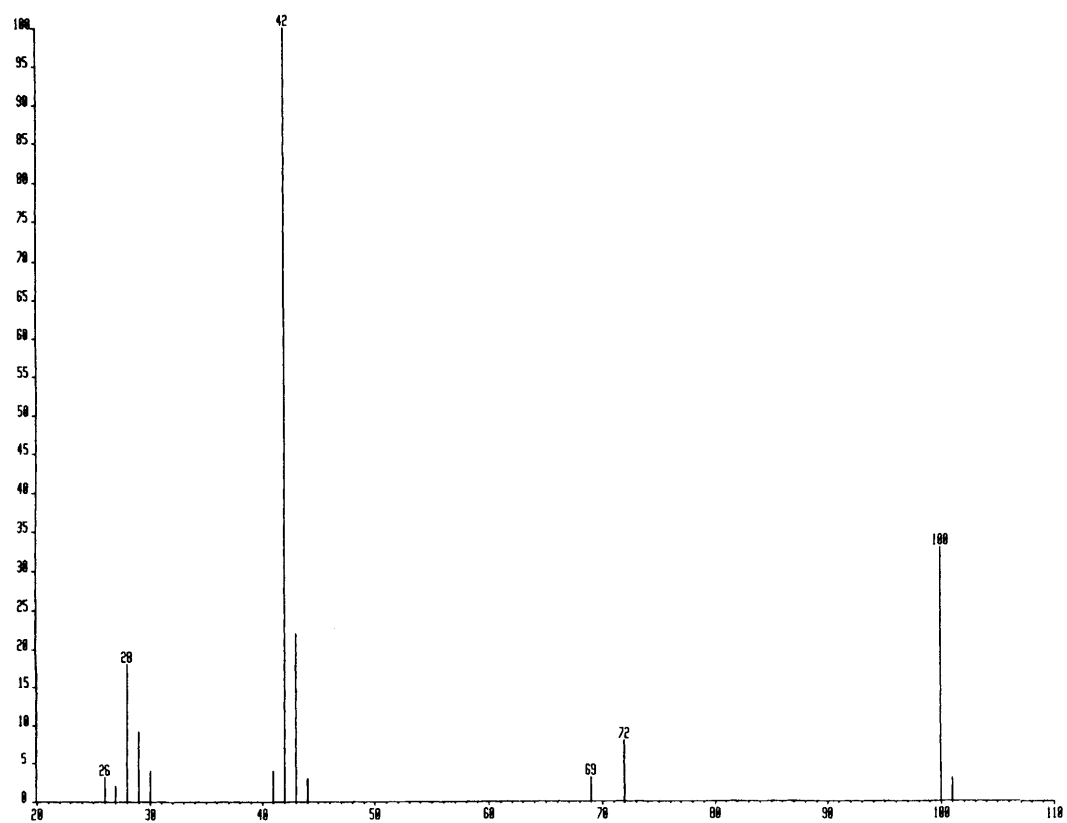
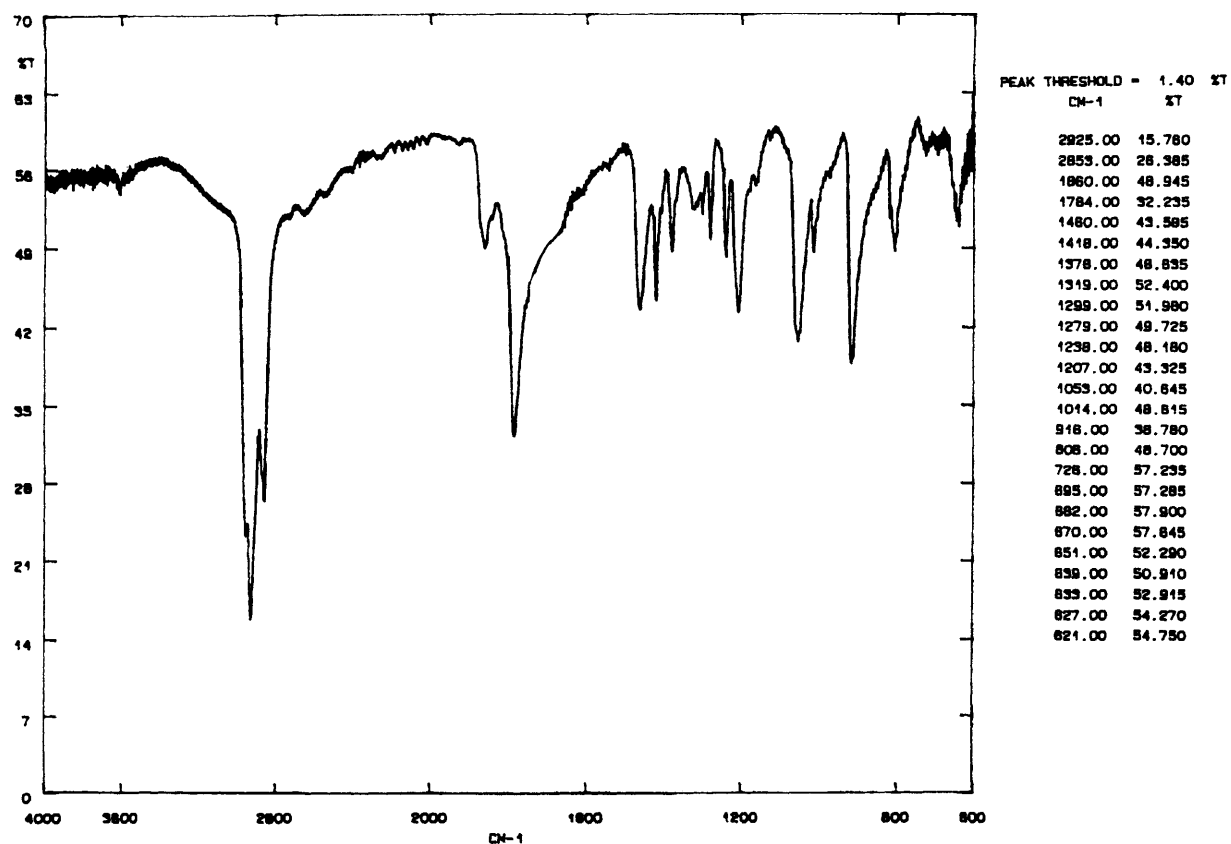
Sample 13.6 *Continued*



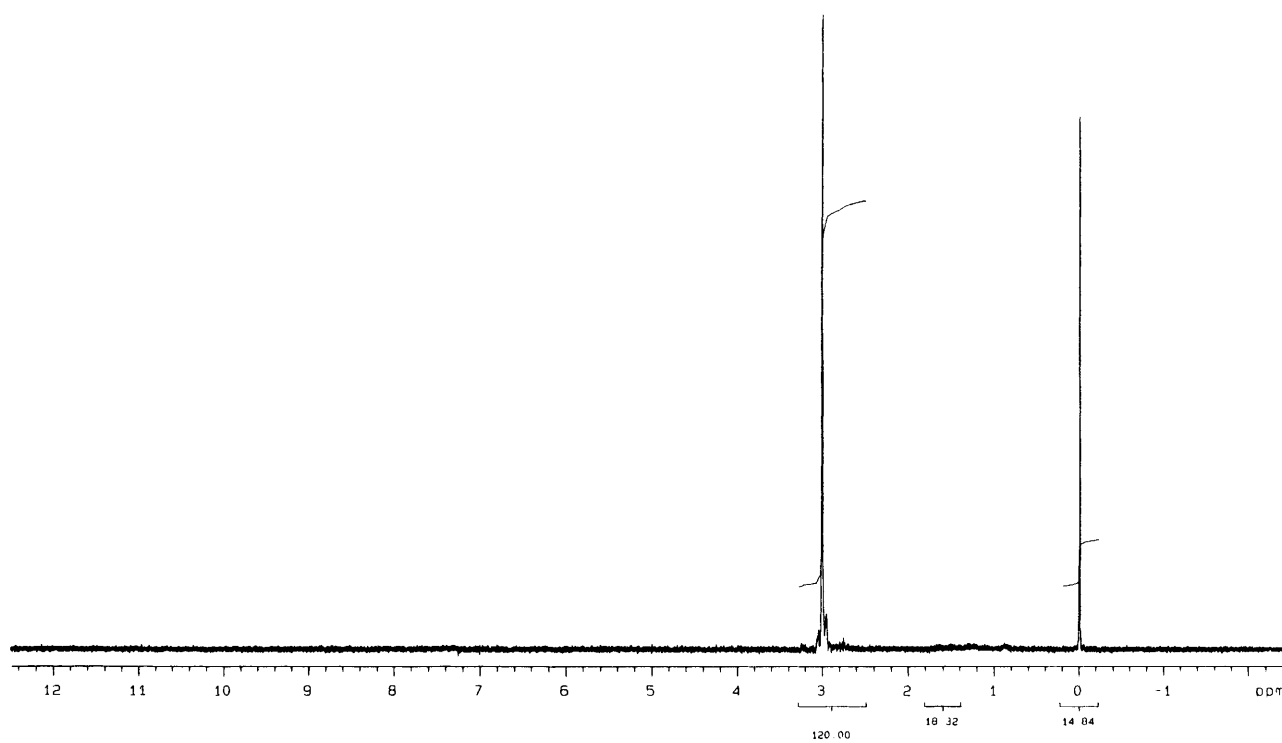
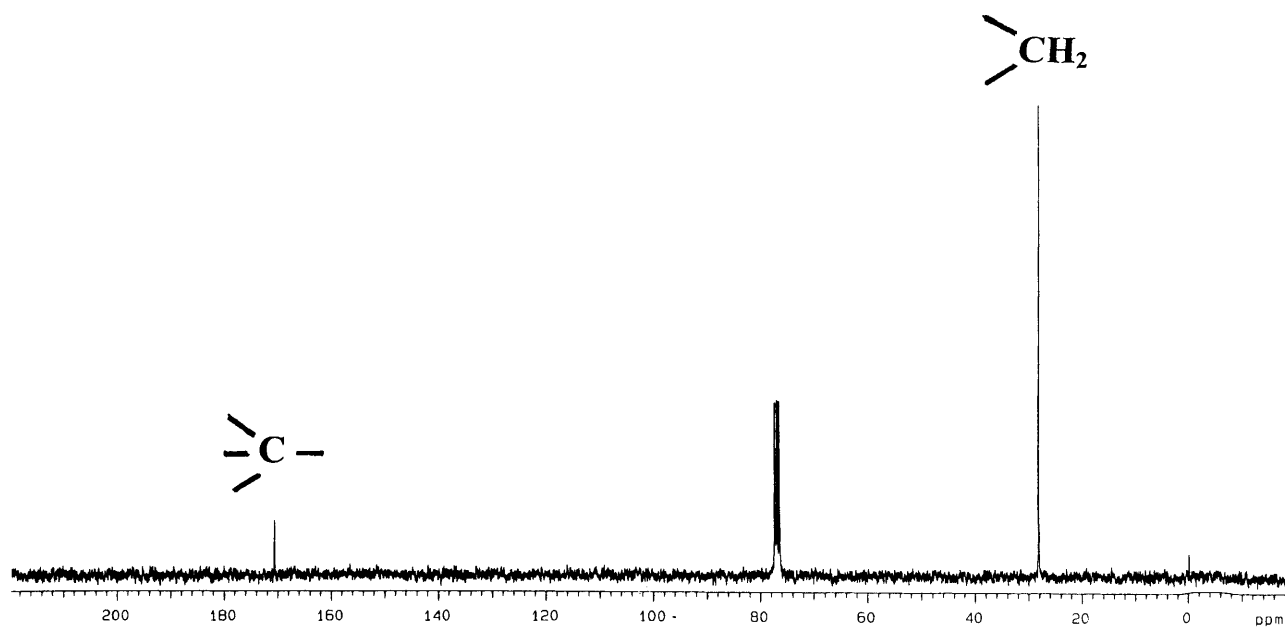
Sample 13.7



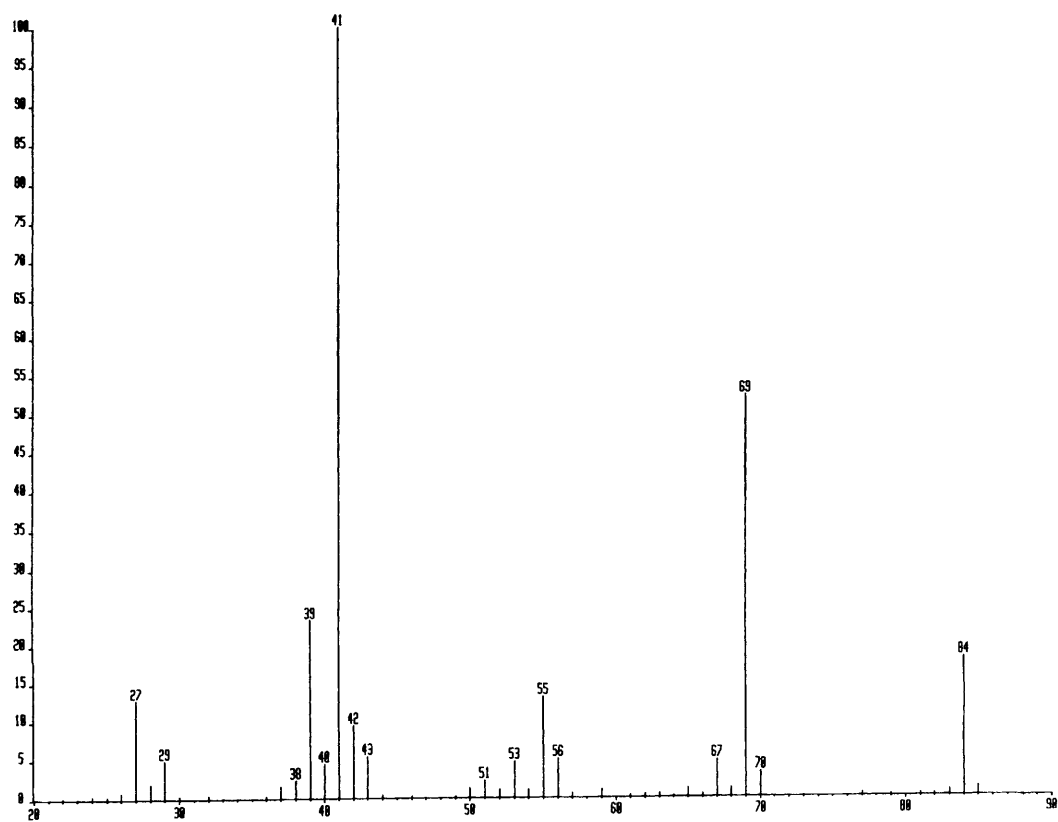
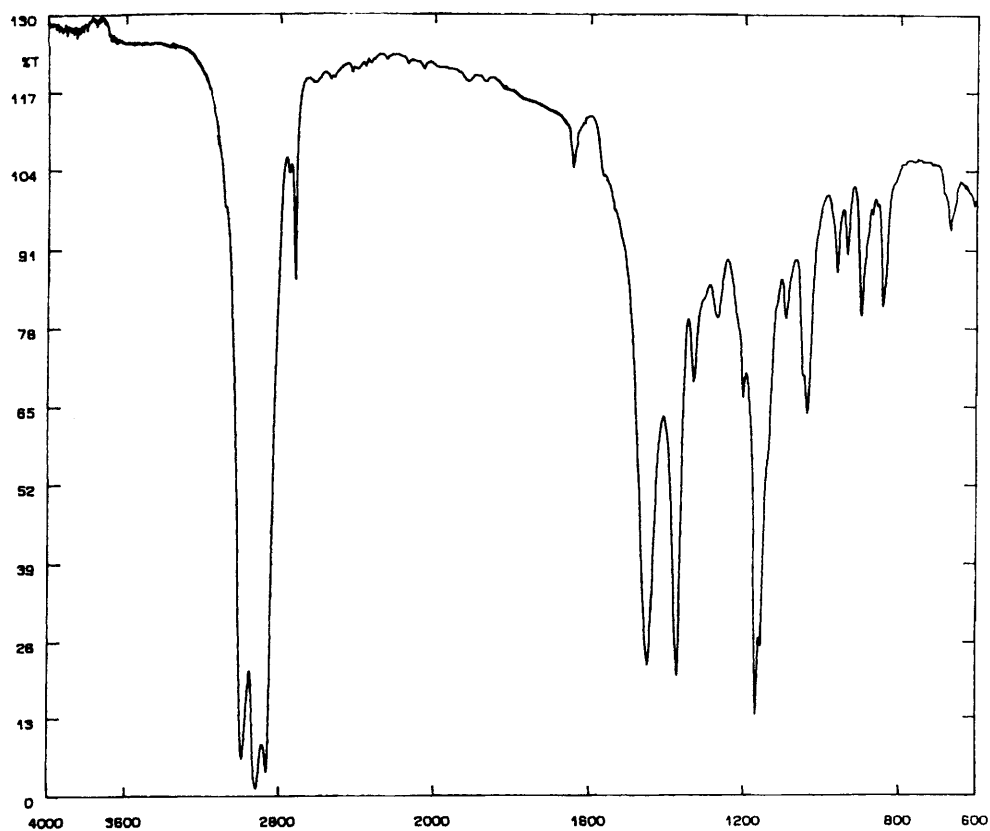
Sample 13.7 Continued



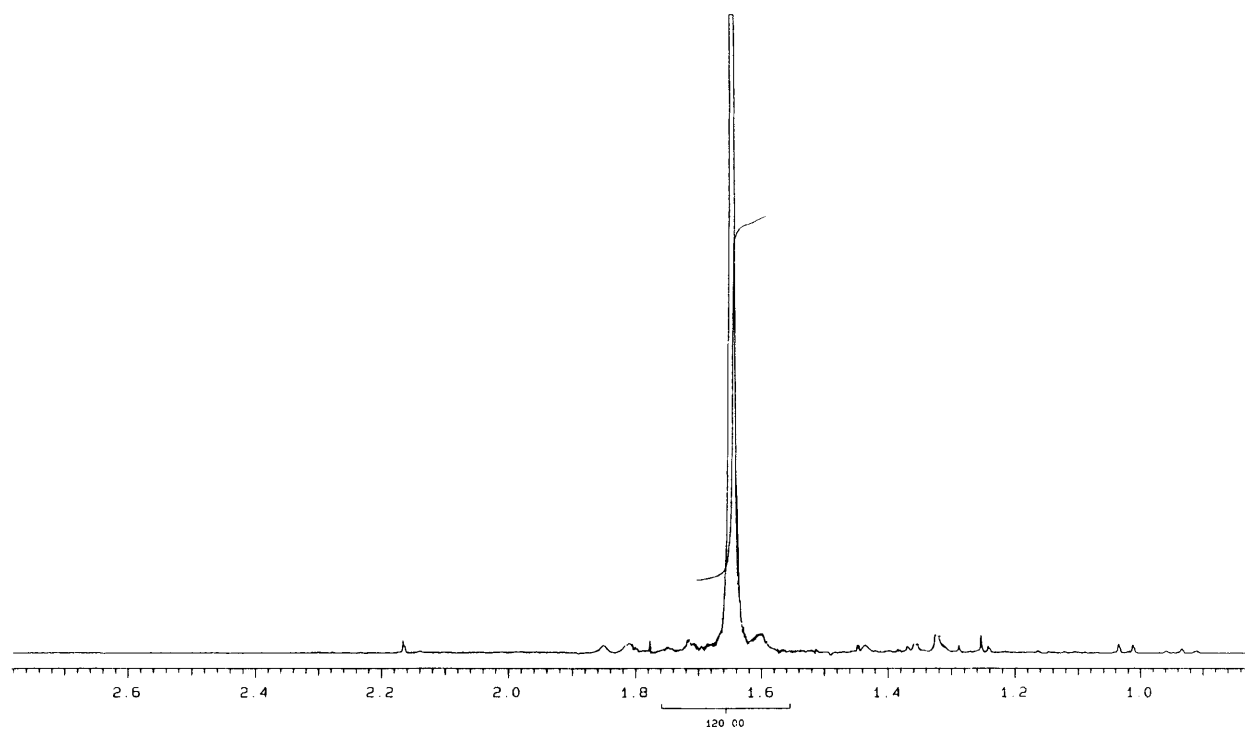
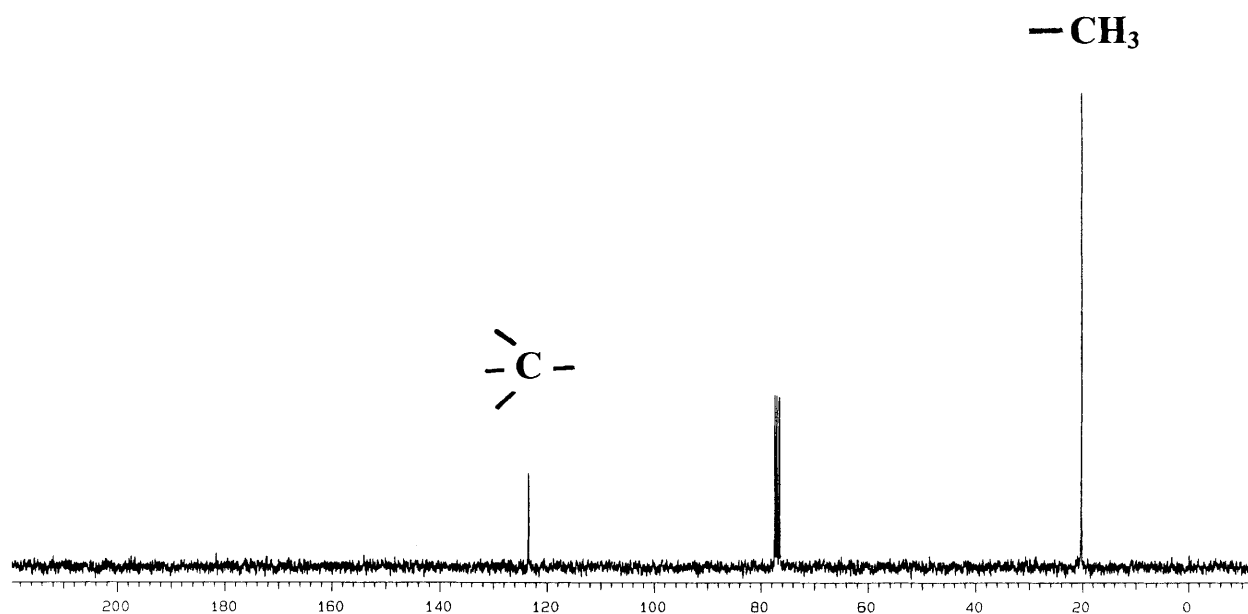
Sample 13.8



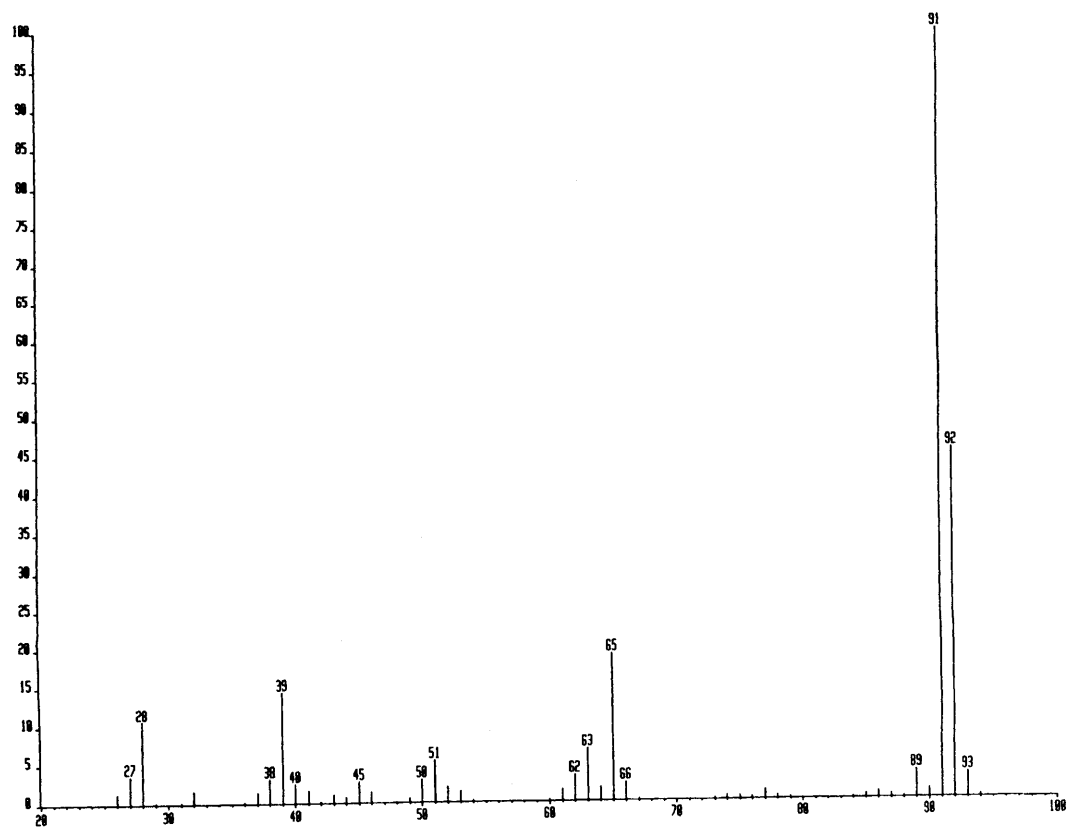
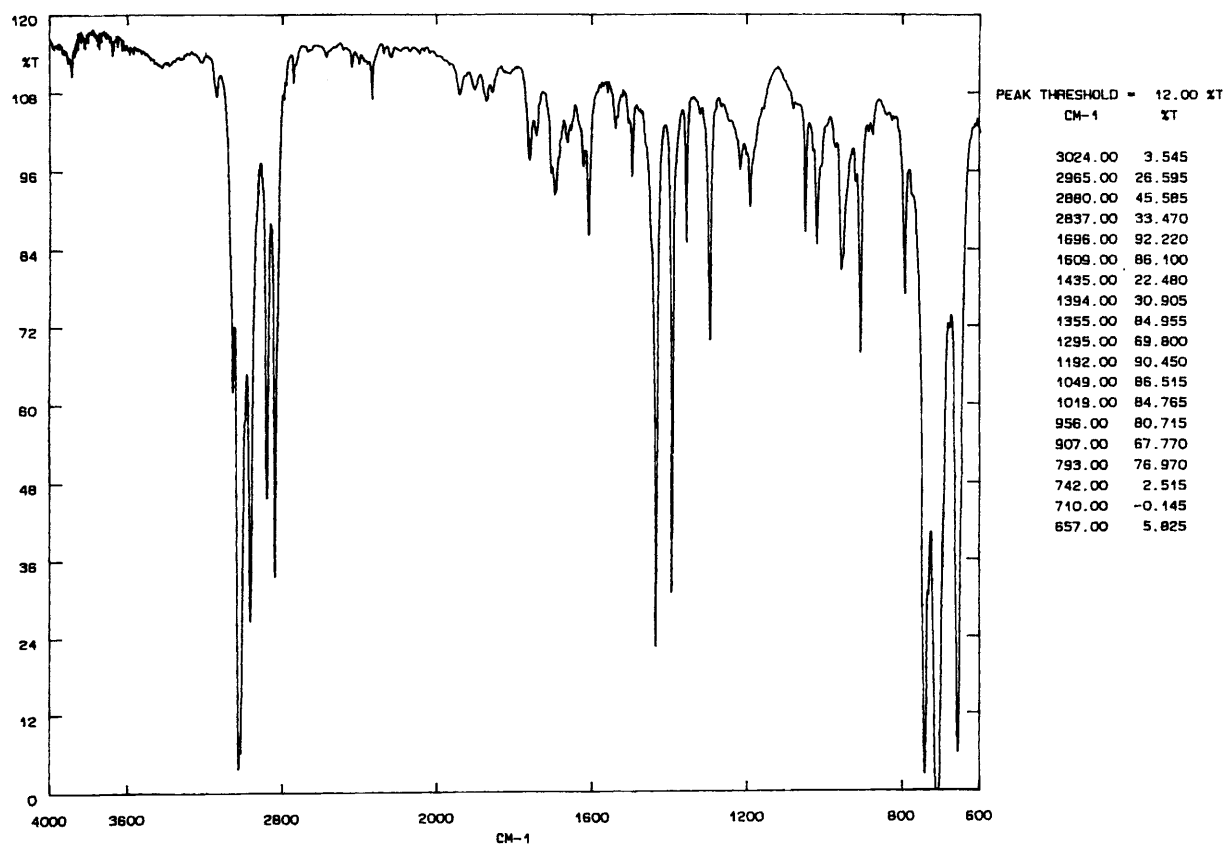
Sample 13.8 Continued



Sample 13.9

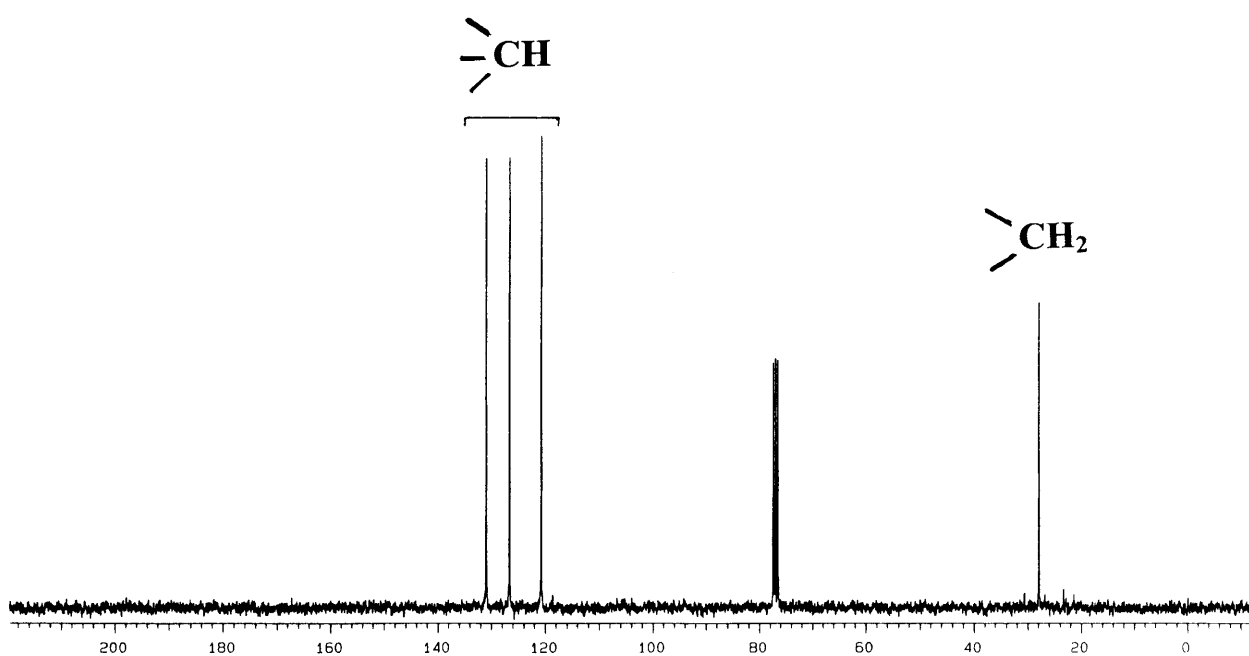
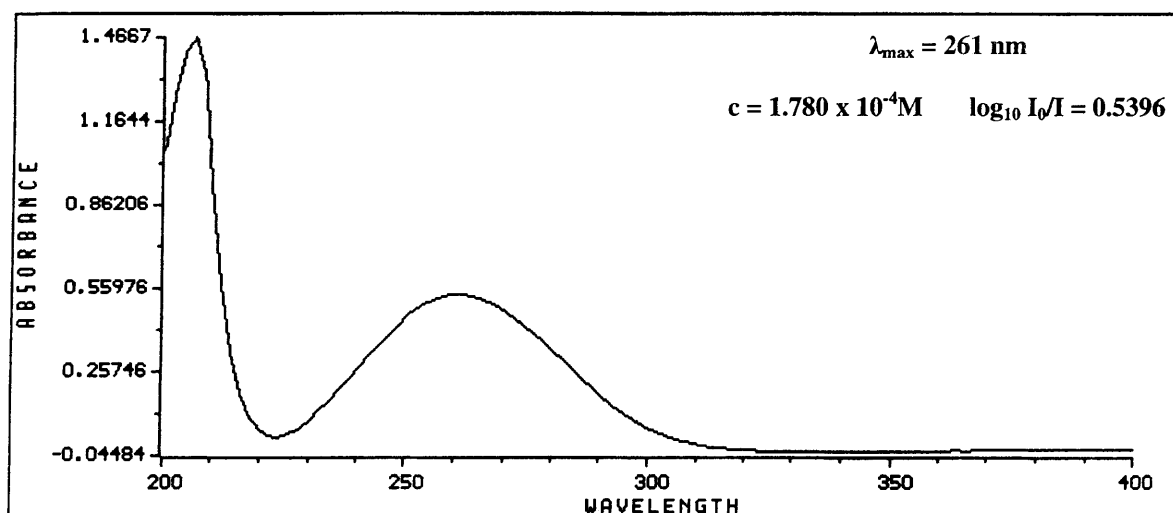


Sample 13.9 Continued

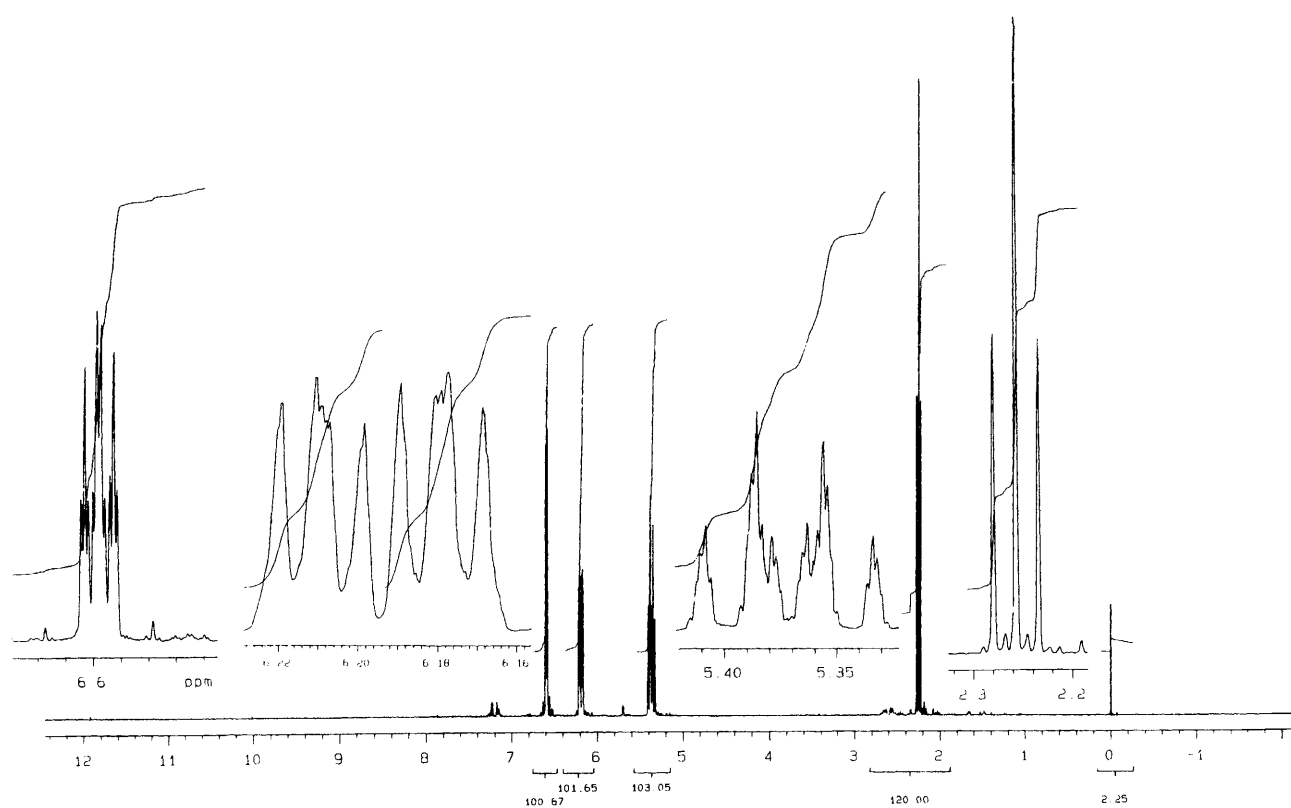


Sample 13.10





Sample 13.10 Continued

**Sample 13.10** *Continued*

## Answers to Problems

### Answers to Chapter 1 Problems

1. Alcohol
2. Ester of saturated acid
3. Primary amine
4. Saturated carboxylic acid
5. Saturated ketone
6. Alkene
7. Anhydride of saturated carboxylic acid
8. Alkynol
9. Ester of unsaturated acid
10. Aromatic carboxylic acid
11. Nitrile
12. Chloride of saturated acid
13. Secondary amide
14. Aromatic ketone
15. Saturated aldehyde
16. Anhydride of aromatic carboxylic acid
17. Chloride of aromatic acid
18. Aromatic aldehyde
19. Unsaturated ketone
20. Tertiary amide

### Answers to Chapter 2 Problems

1. Phenylmethyl bromide (benzyl bromide)
2. Iodoethane
3. Hexane
4. Butanoic acid (butyric acid)
5. 2-Chloropropane
6. Bromoethane
7. Butylbenzene
8. Ethyl butanoate (ethyl butyrate)
9. 2-Aminopropane
10. Phenylmethyl chloride (benzyl chloride)
11. Methyl butanoate (methyl butyrate)
12. Butan-2-ol (*sec*-butyl alcohol)
13. 2-Chloroethylbenzene
14. Butanal (butyraldehyde)
15. Butan-2-amine (*sec*-butylamine)
16. 1,2-Dibromoethane
17. 1,1-Dibromoethane

18. Butanamide (butyramide)
19. (2-Aminoethyl)benzene
20. Hexan-2-one

### Answers to Chapter 3 Problems

1. Propan-2-one (acetone)
2. Ethanol
3. 2-Bromoethanol
4. Acetonitrile
5. Benzaldehyde
6. Ethanoic acid anhydride (acetic anhydride)
7. Ethanoic acid (acetic acid)
8. Methyl acetate
9. Chloroacetonitrile
10. Pentan-3-one

### Answers to Chapter 4 Problems

1. Saturated ketone
2. Unsaturated ketone
3. Unsaturated ketone
4. Unsaturated ketone
5. Triene

### Answers to Chapter 5 Problems

1. Ethanol
2. Propanoic acid (propionic acid)
3. Propan-2-ol (isopropyl alcohol)
4. Methyl benzoate
5. 2-Methylbutane
6. Cyclohexene
7. 2-Phenylethanol
8. *N,N*-Diethylphenylamine (diethylaniline)
9. Di-*n*-butyl ether
10. Propylbenzene

### Answers to Chapter 6 Problems

1. Propan-2-yl acetate (isopropyl acetate)
2. Butanenitrile (butyronitrile,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ )
3. Phenyl acetate
4. Butane-2,3-diol
5. Prop-2-enyl acetate (allyl acetate,  $\text{CH}_2=\text{CHCH}_2\text{OCOCH}_3$ )
6. Benzoyl cyanide ( $\text{PhCOCN}$ )
7. 3,3-Dimethylbutanal (3,3-dimethylbutyraldehyde)
8. Hexanedicarboxylic acid (adipic acid)
9. 2,2-Dimethylpropane-1,3-diol
10. 2-Ethylbutan-1-ol

### Answers to Chapter 7 Problems

1. 1,2-Dimethoxyethane

2. 1-Bromobutane
3. 1,1-Dimethylethylbenzene (*tert*-butylbenzene)
4. Octanal
5. Phenylmethanol (benzyl alcohol)
6. Heptanoic acid
7. 1,1-Dimethylethyl iodide (*tert*-butyl iodide)
8. Bis(1-methylethyl) ether (diisopropyl ether)
9. Cyclohexanone
10. Oct-1-ene

### Answers to Chapter 8 Problems

1. Pentan-2-ol
2. 1,6-Dibromohexane
3. 3-Bromopropanenitrile (3-bromopropionitrile,  $\text{BrCH}_2\text{CH}_2\text{CN}$ )
4. 1-Phenylpropan-1-one (propiophenone)
5. Butan-1-amine (*n*-butylamine)
6. Cycloheptanone
7. Octanoic acid
8. Methyl prop-2-eneoate (methyl acrylate,  $\text{CH}_2=\text{CHCOOCH}_3$ )
9. Methylenecyclohexane
10. Methyl hexanoate
11. 4-Methylpentan-1-ol
12. 1-Methylcyclohexanol
13. Hex-1-en-3-ol
14. 3-Chloropropan-1-ol
15. Heptan-2-one
16. 4-Methoxybenzaldehyde
17. 1-Methylcyclohexene
18. But-3-en-2-one (methyl vinyl ketone)
19. 2-Methylpentanoic acid
20. Cyclohex-2-en-1-one

### Answers to Chapter 9 Problems

1. *N,N*-Diethylphenylamine (diethylaniline)
2. Propan-2-yl acetate (isopropyl acetate)
3. 2-Bromoethanol
4. 2-Phenylethanol
5. *cis*-3-Chloroprop-2-enoic acid (*cis*-chloroacrylic acid)
6. 4-Methoxybenzaldehyde
7. 3-Bromopropanenitrile (3-bromopropionitrile,  $\text{BrCH}_2\text{CH}_2\text{CN}$ )
8. *trans*-3-Chloroprop-2-enoic acid (*trans*-chloroacrylic acid)
9. 1-Phenylpropan-1-one (propiophenone)
10. 3-Nitrobenzoic acid

### Answers to Chapter 10 Problems

1. 2-Methylpropanenitrile (isobutyronitrile)
2. 2-Methylpropanoic anhydride (isobutyric anhydride)
3. Diethylamine
4. Pentan-3-one
5. 3-Phenylpropanal (3-phenylacetaldehyde)
6. Ethyl phenylacetate

7. Propanoic acid (propionic acid)
8. Butanenitrile (butyronitrile)
9. Pentan-2-one
10. 1-Methylethyl benzoate (isopropyl benzoate)

### Answers to Chapter 11 Problems

1. Diethyl ether
2. 1-Iodobutane
3. Ethylbenzene
4. 2-Chloropropane
5. 1,3-Dichloropropane
6. 1-Methoxy-4-methylbenzene (*p*-methylanisole)
7. Diethyl dipropionate (diethyl malonate)
8. Di-*n*-propyl ether
9. 2-Methylbutane (isopentane)
10. 2,2-Dimethylpropane-1,3-diol

### Answers to Chapter 12 Problems

1. Butan-2-one
2. 2-Methylpropan-1-yl acetate (isobutyl acetate)
3. Propanenitrile (propionitrile,  $\text{CH}_3\text{CH}_2\text{CN}$ )
4. 1-Phenylethanone (acetophenone)
5. Prop-2-yn-1-ol (propargyl alcohol)
6. 3-Methylbutan-2-one
7. Tripropylamine
8. Heptan-3-one
9. Butylbenzene
10. 4-Bromobenzaldehyde
11. Diethyl ethanedioate (diethyl oxalate)
12. 4-Methylpentan-2-one
13. *N,N*-Diethylformamide
14. Methyl 2,2-dimethylpropanoate
15. 1-(4-Bromophenyl)ethanone (4-bromoacetophenone)
16. 2-Methylpropylbenzene (isobutylbenzene)
17. Ethyl cyanoacetate
18. Diethyl butanedioate (diethyl succinate)
19. 4-Bromobutanenitrile (4-bromobutyronitrile)
20. 4-Methylpent-3-en-2-one (mesityl oxide)

### Answers to Chapter 13 Problems

1. Ethyl methoxyacetate
2. Propen-2-yl acetate (isopropenyl acetate)
3. 1,3,5-Trimethylbenzene
4. Cyclododecane
5. Ethyl *trans*-3-phenylprop-2-enoate (*trans*-ethyl cinnamate)
6. 1,4-Dimethoxybenzene
7. Diethyl ethylpropanedioate (diethyl ethylmalonate)
8. Butanedioic anhydride (succinic anhydride)
9. 2,3-Dimethylbut-2-ene
10. Cycloheptatriene

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Spectroscopic data undoubtedly provide a great deal of useful information about organic molecules. Competently deriving structural information from such data therefore, is a requisite skill for many undergraduates studying chemistry. *Interpreting Organic Spectra* covers the basic principles of spectroscopy in as non-mathematical a way as possible. It assumes no previous knowledge of spectroscopy and avoids excessive theory, approaching the topic as an exercise in pattern recognition. Hence the main focus of the book is in the provision of a variety of spectra for the student to interpret. Students are able to pace their progress by gaining confidence on the simpler spectra, and applying techniques learned to tackle more complex examples. As an introduction to the subject, it is ideal for A-level students as well as chemistry undergraduates and will prove to be a very useful reference tool for teachers and lecturers.



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